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DETERMINATION OF KINETIC EQUATIONS OF ALKALINE ACTIVATION OF BLAST FURNACE SLAG BY MEANS OF CALORIMETRIC DATA

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Abstract

The alkaline activation of blast furnace slag promotes the formation of new cement materials. These materials have many advantages over ordinary Portland cement, including high strength, low production cost and good durability. However, many aspects of the chemistry of alkaline activated slags are not yet very well understood. Some authors consider that these processes occur through a heterogeneous reaction, and that they can be governed by three mechanisms: a) nucleation and growth of the hydrated phase; b) phase boundary interactions and c) any diffusion process though the layer of hydration products.

The aim of this paper was to determine the mechanism explaining the early reaction of alkaline activation of a blast furnace slag through the use of calorimetric data.

A granulated blast furnace slag from Avilés (Spain) with a specific surface of 4450 cm^2 g^{-1} was used. The alkaline activators used were NaOH, Na_2CO_3 and a mix of waterglass ($Na_2SiO_3 \cdot nH_2O$ and NaOH. The solution concentrations were constant (4% Na_2O with respect to the slag mass). The solutions were basic (pH 11–13). The mixes had a constant solution/slag ratio of 0.4.

The thermal evolution of the mixes was monitored by conduction calorimetry. The test time was variable, until a rate of heat evolution equal to or less than 0.3 kJ kg^{-1} h^{-1} was attained. The working temperature was 25°C.

The degree of hydration (α) was determined by means of the heat of hydration after the induction period. The law governing the course of the reaction changes at a certain degree of hydration. From a generally accepted equation, the values of α at which the changes are produced were determined. These values of α depend on the nature of the alkaline activator. Nevertheless, for high values of α, the alkaline activation of slag occurs by a diffusion process.

Keywords: activation, alkaline, blast furnace slag, kinetic, mechanisms

Introduction and theoretical background

Cements and concretes from alkaline activated blast furnace slags (BFSs) have been studied by a large number of authors [1–6]. As compared to ordinary Portland cement, these cements and concretes are characterized by advantages such as higher mechanical strength, lower hydration heat, better impermeability, better behaviour upon carbonation, better resistance to high temperatures, higher

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resistance to chemical attack and to aggregate-matrix interphase, greater protection to concrete reinforcement, biocide and bacteriological resistance, etc. These cements and concretes also have some disadvantages relative to ordinary Portland cements, such as faster setting, higher microcrack formation and strength variation.

The alkaline activation of BFS is a complex process [6] in which the BFS structure is first broken down, followed by a polycondensation and precipitation of the reaction products formed. Some authors [7–10] consider this process to occur through a heterogeneous reaction. Such reactions are governed by three mechanisms: a) nucleation and growth of hydrated phases, b) phase boundary interactions and c) diffusion through a hydration product layer.

A nucleation process occurs on a solid surface. When the nuclei are randomly distributed around the grain surface, the interactions between them stop their growth; in these cases, the process is controlled by the Avrami-Erofe'ev [11] equation (1). If the nuclei of the products formed are uniformly distributed on the solid surface, a reacting interphase is rapidly formed and the process will be governed by phase boundary Eq. (2). The diffusion process occurs through a reaction product layer that surrounds the anhydrous BFS. The equation that best explains this diffusion process is that of Jander [12] (3). This Jander equation is valid when the ratio of the width of the hydration product layer and the radius of the initial particles (R) is lower than 0.5, involving a low conversion degree of the initial particles [13]. In most of the systems, mechanisms evolve from A_1 to D_3.

$$A_1(\alpha) = [-\ln(1-\alpha)]^{1/n} = K_1 t = K_1' t \tag{1}$$

$$D_2(\alpha) = [1-(1-\alpha)^{1/3}] = K_2 R^{-1} t = K_2' t \tag{2}$$

$$D_3(\alpha) = [(1-(1-\alpha)^{1/3})^2] = k_3 R^{-2} t = k_3' t \tag{3}$$

α=hydration degree; K=constant; R=particle radius; t=time.

When α is differentiated with respect to t in expressions (1) (2) and (3), rate constants of the three processes are obtained [10], the equations being as follows:

$$d\alpha/dt = F_1(\alpha) = K_1 n(1-\alpha)[-\ln(1-\alpha)]^{n-1/n} \tag{4}$$

$$d\alpha/dt = F_2(\alpha) = 3K_2 R^{-1}(1-\alpha)^{2/3} \tag{5}$$

$$d\alpha/dt = F_3(\alpha) = 3/2[K_3 R^{-2}(1-\alpha)^{2/3}]/[1-(1-\alpha)^{1/3}] \tag{6}$$

$F_1(\alpha)$ represents a nucleation process (4), $F_2(\alpha)$ a process of phase boundary interactions (5) and a diffusion process (6).

Figures 1a and 1b depict theoretical curves representing the three main processes that could take place in a heterogeneous reaction in the solid state [10].

The points of intersection of the curves correspond to the hydration degrees of the particle from which the law governing the hydration process changes. In Fig. 1a, the process proceeds by nucleation until α_1, followed by a phase boundary interaction until α_2, where a diffusion process starts. In Fig. 1b, the reaction occurs through nucleation and diffusion exclusively, α'_1 being the hydration degree for which the change from one mechanism to another is produced.

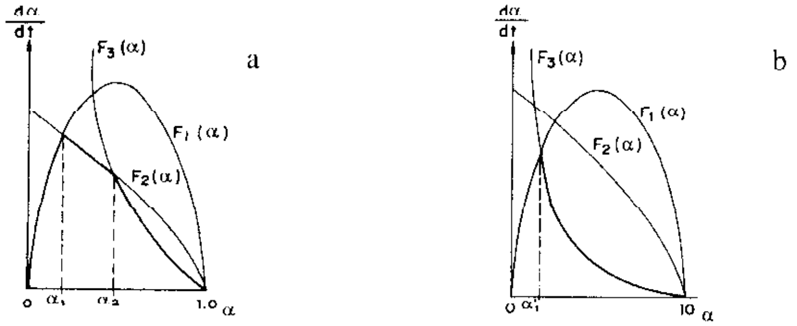

Fig. 1 Relationship between rate of hydration ($d\alpha/dt$) and α for a) a reaction proceeding in three steps and b) a reaction proceeding in two steps

Few works have been published which report kinetic studies of the alkaline activation of a BFS. From calorimetric data, the authors of the present work recently determined that, after the induction period is finished in the rate of heat evolution curves, the mechanism explaining the alkaline activation of a BFS is mainly diffusion; the Jander equation [14] best fits the experimental results [15].

Taking into account the theoretical considerations described above, the aim of the present work was to confirm whether or not nucleation and phase boundary processes occur before a diffusion process under the conditions indicated (after the induction period). The influence of the nature of the alkaline activator on the kinetics of these processes has been studied.

Experimental

Raw materials

BFS from the ENSIDESA factory (Avilés-SPAIN) was used in this work. Its chemical composition and specific surface are detailed in Table 1. Three different alkaline activators were used: NaOH, Na_2CO_3 and a mixture of waterglass ($Na_2SiO_3 \cdot nH_2O$) and NaOH. Solution concentrations were constant (4% of Na_2O by mass to the BFS). The solutions were basic [11–13].

Table 1 Chemical composition of blast furnace slag (%wt)

CO_2	R. Insol	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	S^{2-}	I.B. (F_3)	Specf. surf.
1.23	0.14	36.10	11.22	0.49	42.80	8.40	0.71	1.72	4480 cm^2 g^{-1}

Mixes of activator solution/BFS were prepared with a constant mass ratio of 0.4. These mixes were studied by means of conduction calorimetry (calorimeter model J. A. F.). The test time was variable, until the rate of heat evolution reached a value equal to or less than 0.3 kJ kg^{-1} h^{-1}. The working test temperature was 25°C.

Results and discussion

Rate of heat evolution

The rate of heat evolution curve of an alkaline activated BFS [16] is characterized by the presence of five steps. The first step is associated with the first peak of the curve. It corresponds to the first few minutes of reaction and is assigned to partial dissolution of the BFS. The second step corresponds to a period called the induction period, in which the rate is low; it is a consequence of a period of low reactivity. The third and fourth steps are associated with the second peak. In these steps, a massive precipitation of reaction products occurs. These steps are usually called acceleration and deceleration, respectively. Finally, the fifth step corresponds to a low reactivity period called decay or completion of the reaction.

Different parameters such as reaction temperature, activator concentration and BFS specific surface alter the intensity and duration of the steps [14–17]. From the results obtained and presented in Fig. 2, where the nature of the activator was varied at constant concentration (4% Na_2O with respect to the slag mass),

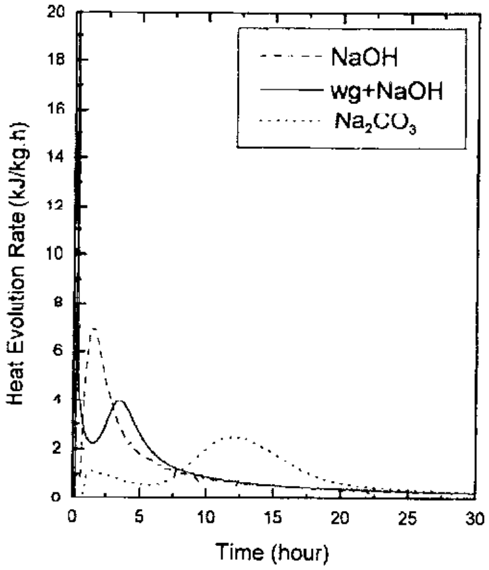

Fig. 2 Rate of heat evolution *vs. t*

it is deduced that the nature of the activator may modify these steps. The reaction between slag and alkaline solutions is initially very fast and intense and makes it difficult to observe the first signal (first step) in the three cases. The second step, associated with the induction period, is also affected by the nature of the activator. This period is short when NaOH is the activator, Na_2CO_3 producing the longest induction period.

Table 2 Rate and hydration heat for alkaline activated slag

Mixes	Activator	Rate 2nd peak (V_2max)/ kJ kg^{-1} h^{-1}	Time (V_2max)/ h	Q'max/ kJ kg^{-1}
1	NaOH	7.005	1.43	115.00
2	wg+NaOH	3.96	3.43	130.95
3	Na_2CO_3	2.50	12.06	148.00

The second peak in the curve of rate of heat evolution is also modified by the nature of the activator. This second peak is associated with the massive formation and precipitation of hydration products, mainly hydrated calcium silicates of the C S H gel type [17, 18]. Table 2 lists the values of heat evolution rate (kJ kg^{-1} h^{-1}) for the second peak together with the time (h) at which the signal appear. When the BFS is activated with NaOH, the second peak of the rate curves appears to be more intense and to occur at shorter times than when other activator solutions are used. Thus, with Na_2CO_3 the signal appears after longer times (about 12 h) and with considerably lower intensities.

Hydration heat

The hydration heat is obtained when the rate of evolution curve is integrated. To determine the hydration heat, we considered that the first peak, associated with the early dissolution process, is obtained very fast and it is not always possible to detect it properly. Likewise, it is considered that the induction period makes a small contribution to the total heat. A new heat of hydration $Q'(t')$ was defined. This is the heat released from the second peak of the rate of evolution curves. This is the heat released after the induction period [14].

Figure 3 depicts $Q'(t')$ *vs*. t', where t' is the time from which the $Q'(t')$ values were taken. It can be observed that the highest value corresponds to BFS activation with NaOH. The order of the curves is the same as obtained for the rate of evolution curves.

Degree of hydration

The degree of hydration, α, was determined by using the Schutter and Taerwe [19] equation (7). For this, it is necessary to know the value of Q' max:

$$\alpha = Q'(t)/Q'\text{max} \tag{7}$$

Q'max is the total or maximum heat released when the reaction has been completed. Q'max was obtained according to the Knudsen extrapolation equation (8) [20]. This is done by considering maximum heat values for rate values equal to or lower than 0.3 kJ kg^{-1} h^{-1}. The values of Q'max obtained are given in Table 2.

$$1/P = 1/P_i + (t_{0.5}/P_i) \times (1/t) \tag{8}$$

where $P=Q'(t')$, $P_i=Q'$max and $t_{0.5}$ is the time necessary for 50% of the total heat to be released.

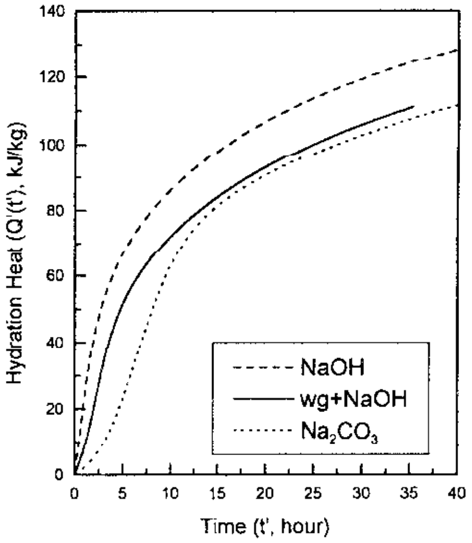

Fig. 3 Hydration heat, $Q'(t')$ *vs.* t'

The extrapolated value of Q'max is highest for the BFS activated with Na_2CO_3. The lowest value was obtained for the BFS activated with NaOH (Table 2). The order obtained $Q'(t')$ is different from that obtained for V_2max. This occurs because the reaction of the BFS with NaOH is very fast and a large amount of heat is released in the first few hours; later, the process decelerates, probably due to the formation of reaction products of high density. When the activator is Na_2CO_3, the reaction is initially slower, but it speeds up with time, reaching total heats higher than those obtained with the other two activators. Further products of a different chemical nature and thermodynamic stability are formed [10, 17].

The hydration degree (α) values represented as a function of time (t') are shown in Fig. 4. The BFS activated with NaOH has the highest α value at short time.

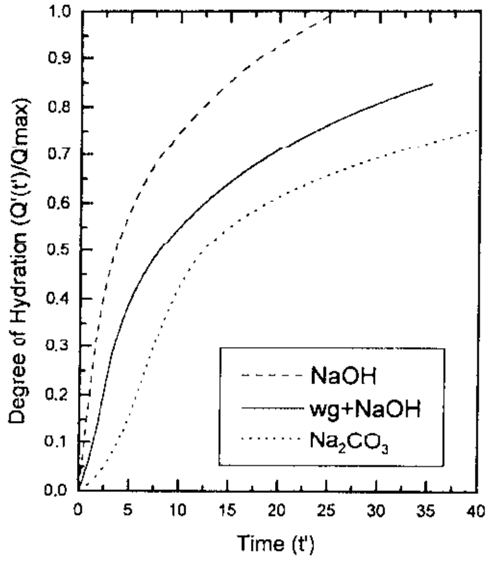

Fig. 4 Degree of hydration *vs.* t'

It must be noted that the α values obtained with this procedure are not real reaction degrees, as for example those obtained with the methanol-salicylic acid method [17]. However, these hydration degree values are perfectly valid for following the kinetics of the early process for alkaline activated BFS.

Determination of hydration mechanism

In order to determine the law governing the processes of the early hydration of BFS, like the hydration degree for which this law changes, the hydration rate (w) was represented *vs.* the hydration degree (α). The hydration rate or reduced rate, w, is defined as $V(t')/V_2\max$ (where $V_2\max$ corresponds to the rate of the second peak in the rate of heat evolution curves, and $V(t')$ is the rate of hydration heat evolution as a function of time from the beginning of the second peak). The hydration rate (w) is proportional to $d\alpha/dt$ [21].

In Fig. 5, w *vs.* α is represented for the three mixes studied. It is observed how the BFSs activated with NaOH and waterglass + NaOH give curves that are similar in shape, but different from that for BFS activated with Na_2CO_3.

Figures 6, 7 and 8 represent relations between the experimental values and theoretical equations (4) (5) and (6). The relationships were determined by means of a computer program using minimum square adjustment. The values of the intersections of the curves give the α_1 and α_2 values, and the fitting of the equation to the experimental values gives the rate constants. These values are shown in Table 3.

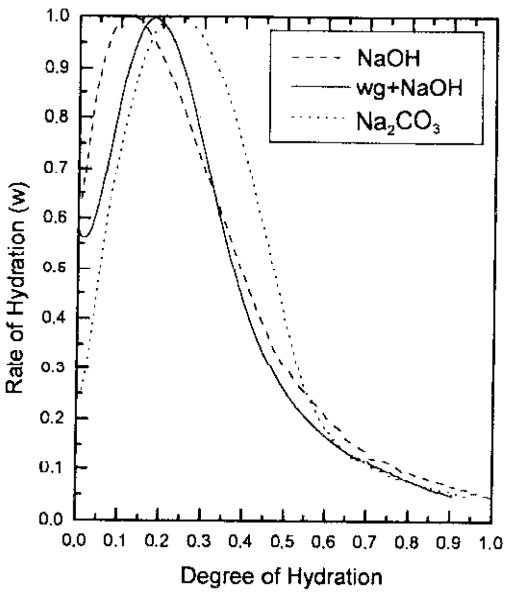

Fig. 5 Rate of hydration *vs.* degree of hydration

From the results obtained in Figs 6, 7 and 8, it is deduced that, once the induction period has finished, the process of alkaline activation of BFS does not go through a diffusion process exclusively. In the first stages, for low hydration degrees, α, nucleation and phase boundary processes are produced, whereas a diffusion process occurs for values of $\alpha > 0.3$.

The nucleation process is completed (for the BFS activated with NaOH) at low α values, but definitely by $\alpha_1=0.09$. With the other activators used in the present

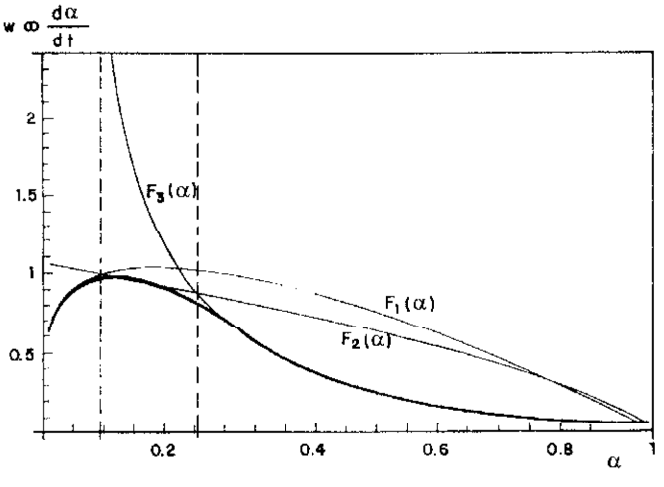

Fig. 6 Rate of hydration *vs.* α for a BFS activated with NaOH

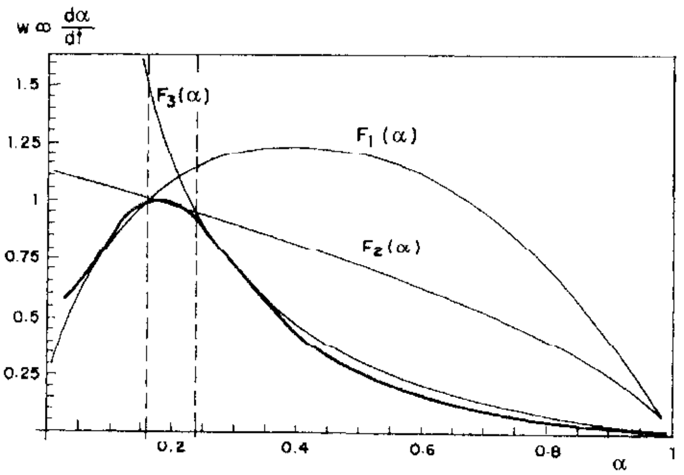

Fig. 7 Rate of hydration *vs*. α for a BFS activated with waterglass + NaOH

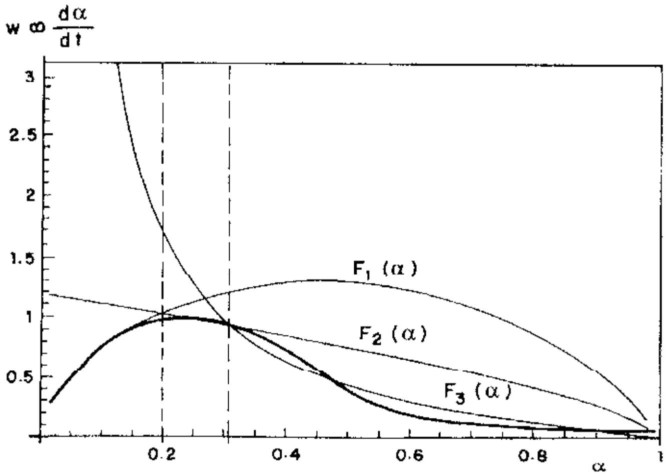

Fig. 8 Rate of hydration *vs*. α for a BFS activated with Na_2CO_3

work, the nucleation process is more extensive, reaching an α_1 value of 0.16 for waterglass + NaOH and an α_2 value of 0.20 for Na_2CO_3.

The α_2 values (indicating the hydration degree for which the law governing the hydration process changes from phase boundary to diffusion) obtained with NaOH and waterglass + NaOH solutions are practically the same (α_2=0.25 and α_2=0.24, respectively). The corresponding value is slightly higher for Na_2CO_3 (α_2=0.30). It is observed how, in the BFS activated with NaOH solution, the nucleation process is considerably shorter and the phase boundary process is enlarged relative to the other alkaline solutions used. This is probably due to the nature and width of the hydration products formed around the BFS grain that remains anhydrous, which vary with the nature of the alkaline solution.

Table 3 also presents n values, n is a parameter indicating the reaction degree when the hydration mechanism is nucleation (Eq. 1 or 4). Thus, for n values of the process will be described by a first-order equation [11] ($F_1=-\ln(1-\alpha)$]. When $n=2$, the nucleation process is explained by the Avrami [22] equation [$A_2=(-\ln(1-\alpha))^{1/2}$]. When $n=3$, the Erofe'ev [23] equation [$A_3=(-\ln(1-\alpha))^{1/3}$] explains the process.

Table 3 Values of kinetic equations

Activator	α_1	α_2	n	K'_1	K'_2	K'_3
NaOH	0.09	0.25	1.2	1.40	0.36	0.066
wg+NaOH	0.16	0.24	2.0	1.43	0.37	0.065
Na_2CO_3	0.20	0.30	2.6	1.25	0.40	0.092

When the BFS was activated with NaOH, a value $n=1.2$ was obtained. This value indicates that the process fits a first order equation, but in this case there is doubt about the reliability of this value. Activation of the BFS with NaOH occurs very rapidly, involving a lack of the initial calorimetric data necessary for the mathematical fitting. The n values obtained for the BFSs activated with waterglass + NaOH and Na_2CO_3 (2.0 and 2.6 respectively) indicate that the nucleation process is described by the Avrami and Erofe'ev equations.

Table 3 includes rate constant values. These values of K'_1, K'_2 and K'_3 (see Eqs (1), (2) and (3)) involve the initial particle radius, which is considered the same for all BFS grains. The BFS samples activated with NaOH and waterglass + NaOH display similar values of K'_1, K'_2 and K'_3 while the BFS activated with Na_2CO_3 presents slightly different values.

Conclusions

The results obtained in the present work, indicate that once the induction period has finished, the alkaline activation of a BFS (4480 cm^2 g^{-1}) with NaOH, waterglass + NaOH and Na_2CO_3 (for a constant concentration, 4% Na_2O with respect to the BFS mass) is governed by three mechanisms: nucleation, phase boundary interactions and diffusion. Of these three processes, diffusion is the predominant mechanism for a hydration degree >0.3.

For a constant activator solution concentration (4% Na_2O with respect to the mass), the nature of the activator solution influences the duration of the different processes controlling the BFS activation. Accordingly, the BFS samples activated with NaOH and waterglass + NaOH exhibit similar behaviour, the diffusion process starts at α_2 values that are practically equal and very similar rate constants (K_1', K_2' and K_3') are obtained. However, the BFS activated with Na_2CO_3 presents a longer nucleation process, diffusion starts at higher α_2 values and the rate constant values are slightly different from those obtained in the other two cases.

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