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ALKALI-ACTIVATED SLAG CEMENTS: KINETIC STUDIES

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ABSTRACT

The kinetics of hydration of alkali-activated slag (AAS) have been studied for different temperatures. The alkaline activator used was a mix of water-glass and NaOH solution. The degree of reaction was determined by means of the heat of hydration after the induction period. The reaction mechanism determined for AAS pastes was a diffusion mechanism and their activation energy was 57.6 KJ/mol. © *1997 Elsevier Science Ltd*

Introduction

The alkaline activation of blast furnace slag is a complex process where the destruction of the slag structure is firstly produced and subsequently a policondensation-crystallization of reaction products occurs. Alkaline activated slag (AAS) cements and concretes have many advantages over ordinary portland cement. Some of these advantages are high strengths, low production cost and good durability (1-3).

However, many aspects of the chemistry of alkaline activated slags hydration are unclear (4-7). The hydration mechanisms that explain the reaction of the slag with an alkaline activator are not very well understood. Huanhai et al. (8) concluded in 1993 that the hydration process of AAS could be classified into five stages (initial, induction, acceleration, deceleration and decay), which is similar to that of OPC, but the mechanisms are different in both cases.

The aim of this paper is the determination of kinetic equations explaining the slag alkaline activation after the induction period. The influence of curing temperature in that reaction kinetics has been studied.

Experimental

1. Raw Materials. Blast furnace slag (BFS) from ENSIDESA factory (Avilés-SPAIN) was used in this work. Its chemical composition and specific surface are shown in Table 1.

Alkaline activator used was a mix of commercial water glass (SiO_2 = 18.01%; Na_2O = 8.53%) and NaOH solution (4.62 N). The alkali modulus of solution (SiO_2/Na_2O ratio) was 1.5, Na_2O concentration was 4% in slag weight and the pH was 13.22.

TABLE 1

Chemical Composition of Blast Furnace Slag (%wt)

	CO_2	Insol	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	I.B. (F_3)	specf.surf.
0,10	1,23	0,14	36,10	11,22	0,49	42,80	8,40	0.0	1.72	4400 cm^2/g

2. Determination of Degree of Reaction. Mixes of activator solution/slag were prepared with a constant weight ratio of 0.4. These mixes were studied by means of conduction calorimetry at the following reaction temperatures: 25, 35, 45 and 60°C. A constant test time was fixed at 45 hours.

The degree of reaction was determined using the Stutter method (9), according to equation [1], where Q(t) is the heat released as a function of time and Qmax is the total or maximum heat released when hydration reactions have been completed.

$$\alpha = Q(t)/Q\max \qquad [1]$$

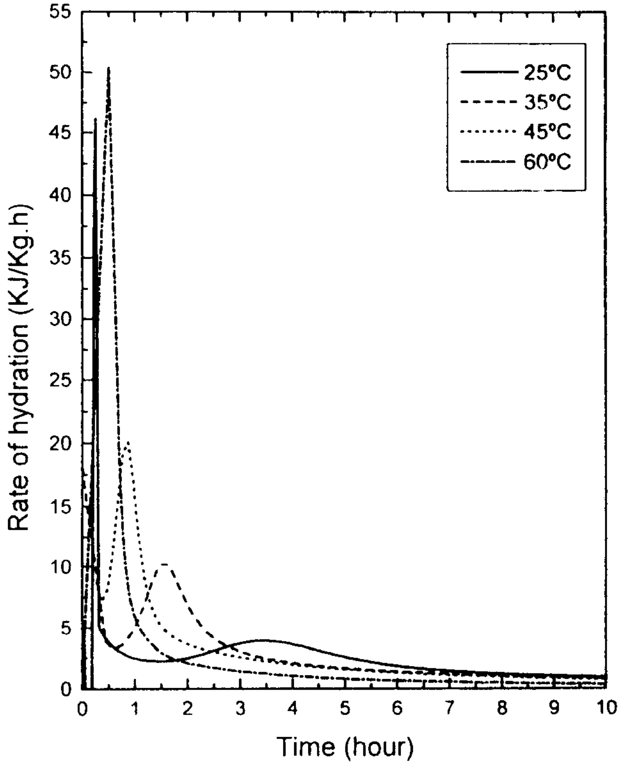

FIG. 1.

Rate of hydration heat vs. t.

In the present study, two different values for Qmax have been determined. These values were called Q'_1 = maximum heat released after 45 hours of isothermal test and Q'_2 = heat obtained extrapolating according to Knudsen equation [2] (10).

$$1/P = 1/P_i + (t_{0.5}/P_i) * (1/t) \qquad [2]$$

where $P = Q(t)$, $P_i = Q'_2$ and $t_{0.5}$ is the time necessary for releasing the 50% of the total heat.

Results and Discussion

1. Degree of reaction. Fig 1. shows rate evolution curves obtained for the different temperatures of study.

In the curve obtained at 25°C five steps can be distinguished, corresponding to those indicated by Huanhai et al. (8). The first step is associated to the first peak of the curve. It corresponds to the first minutes of reaction and it is assigned to the slag partial dissolution. The second step corresponds to a period called induction period in which the rate is low and it is the consequence of a period of low reactivity.

The third and fourth steps are associated to the second peak. In these steps, a massive precipitation of reaction products is produced. These steps are usually called acceleration and deceleration respectively. Finally, a fifth step corresponds to a low reactivity period called decay or finishing of reaction. From experimental data obtained it is deduced that reaction temperature influences the duration and intensity of these steps. When temperature increases, reaction rate is increased and the first peak is not observed with the considerable reduction of the induction period.

In Table 2, the values of hydration heat rate (KJ/Kg.h) for the second peak are shown, likewise the time (hours) at which that signal appears. This second peak is associated to the massive formation and precipitation of hydration products, mainly hydrated calcium silicates of the CSH gel type (7, 11). Hydration heat, Q(t), is obtained when rate evolution curves are integrated. When experimental conditions are taken into account and, considering that the first peak of rate evolution curves could not be detected in all the cases studied, a new heat of

TABLE 2

Rate and Hydration Heat for Alkaline Activated Slag

Temperature (°C)	2nd Peak		Test of 45 hour		Knudsen method	
	Rate (KJ/Kg.h)	Time (hour)	Q'_1 (KJ/Kg)	$t_{1_{0.5}}$ (hour)	Q'_2 (KJ/Kg)	$t_{2_{0.5}}$ (hour)
25	3.96	3.45	119.00	6.40	130.95	7.90
35	10.34	1.54	130.29	4.20	117.00	3.20
45	20.12	0.87	136.06	3.10	112.00	1.80
60	50.45	0.5	86.50	1.60	61.00	0.60

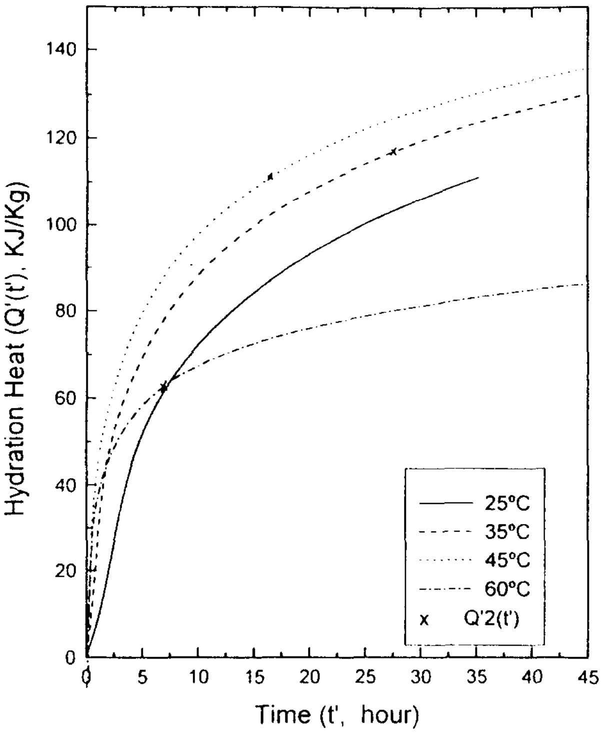

FIG. 2.
Hydration heat, Q'(t), vs. t'.

hydration Q'(t) is defined, as the heat released from the second peak of the rate evolution curves, this is the heat released from the finishing of the induction period.

In Fig. 2, Q'(t) vs. t' is represented, where t' is the time from which Q'(t) values were taken. As temperature increases, hydration heat increases, except for 60°C. At 60°C, in the experimental test conditions, it can be affirmed that a part of the heat released before the induction period finish could not be registered due to the high rate of the process. This justifies the low values of heat obtained at 60°C.

Slag alkaline activation is a fast process as it is seen in the rate evolution curves (the second peak appears at less than 10 hours). Reactions are not completed and they continue at very low rates. This makes very difficult to reached a plate or a constant heat in heat curves and, thus, it is difficult to determine the real value of Q'max. Two methods were evaluated for the determination of Q'max. These methods were the following:

i) A maximum reaction time is fixed. It is constant and the same for all temperatures (Q'1 = heat released at 45 hours of reaction).

ii) To apply Knudsen equation [2], as it was indicated in experimental part. To apply this equation, it must be taken into account that slag reaction is a process enlarged with time. For that reason, a time interval between t' = 0 and t' = t_V (being t_V the time necessary to reach rates lower than 0.3 KJ/Kg.h) was defined. Under these working conditions, the values obtained for Q'2 correspond with the inflexion points of the hydration heat curves (see Fig. 2). The hydration process is not completed and, although heat is being released yet, reaction rates are already very low.

In Table 2, Q'_1 and Q'_2 values are compared. At 25°C, $Q'_1 < Q'_2$, this is due to the lower rate of hydration reactions at this temperature.

At the 45 hours fixed to study the process, the inflexion point in heat curves has not been reached. That Q'_2 value at 25°C was obtained by extrapoling according to Knudsen equation.

For the other temperatures of study, $Q'_1 > Q'_2$. As it was indicated former, slag reaction is a process enlarged with time. Once the time is reached, instead of the appearance of a plate in heat curves, heat curves continue to increase with lower slopes each time. As temperature increases, the inflexion point called Q'_2 appears at times shorter while a residual heat continues to release because reaction has not been completed. This residual heat justifies the differences between Q'_1 and Q'_2 (in both cases, these values were experimentally obtained). In Fig. 2, the points corresponding to Q'_2 at these temperatures are shown.

In Fig. 3, α' values are represented as a function of time (t'). α' values were determined applying equation [3], taking Q'(t) and Q'_2 as heat values.

$$\alpha' = Q'(t)/Q'_2 \qquad [3]$$

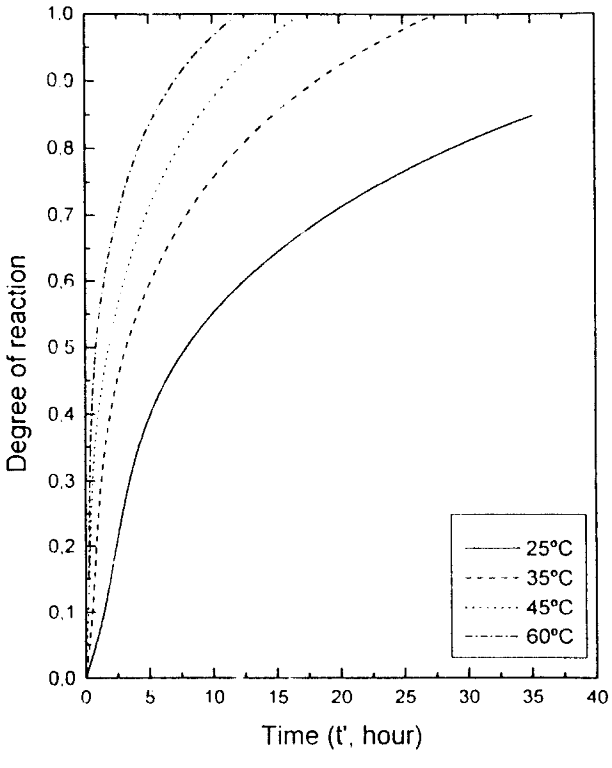

FIG. 3.
Degree of reaction vs. t'.

It must be remarked that α' values obtained through this procedure do not have to coincide with the values determined by other methods, such as the quantification of the anhydrous slag remaining unreacted (11). Heat data provides the evolution of reactions at early ages, although reactions were not completed, as in this case.

Analyzing Fig. 3, it is deduced that as reaction temperature increases, reaction rates are increased. The times necessary to reached the same reaction degrees decrease as curing temperature increases.

To determine kinetic equations explaining alkali-activated slag at the considered steps, the following methods have been applied:

I. Mori and Minegishi method (12). This method is based on equation [4]:

$$(1 - (1 - \alpha)^{1/3})^N = Kt \qquad [4]$$

where, α = degree of reaction; K = rate constant; t = hydration time; N is a value that varies according to the type of reaction governing the process.

Taking logarithms and representing $\log(1 - (1 - \alpha)^{1/3})$ vs. log(t) N value is obtained from the slope (1/N). When $N < 1$, reaction occurs through a nucleation kinetic, when $N = 1$ the process will be governed by a phase boundary kinetic; finally, when $N = 2$, the kinetic correspond to a diffusion process.

In Table 3, N values obtained are shown. At all temperatures studied, N value is between 1, 8 and 2. This is indicating a diffusion kinetic according to Mori and Monegishi.

II. Sharp et al. method (13). Many solid state reactions can be represented by equations of the type $F(\alpha) = Kt$, where α is the fraction of materials reacted in time, t. These equations can be expressed in the form $F(\alpha) = A(t/t_{0.5})$, where $t_{0.5}$ is the time for 50% reaction and A is a calculable constant depending on the form of $F(\alpha)$.

In Fig. 4, α' vs. $t'/t'_{20.5}$ is represented. Similar curves were obtained for the different test temperatures. This means that for this work, all reactions occur through the same mechanism from the acceleration step. Comparing these curves with those described by Sharp et al. (13), it is deduced that they correspond to processes governed by diffusion kinetics, confirming the results described before when the methodology of Mori and Moneghisi is applied.

Slag activation occurs, from the acceleration process, by diffusion. This diffusion occurs through a layer of reaction products surrounding the slag grain still remaining anhydrous. The equations explaining better this diffusion process are those of Jander (14) [5] and Ginstling-Brounshtein (15) [6].

TABLE 3

N Values Obtained Through Equation [4]

	TEST TEMPERATURE			
	25°C	35°C	45°C	60°C
N	1.80	1.94	1.94	2.03

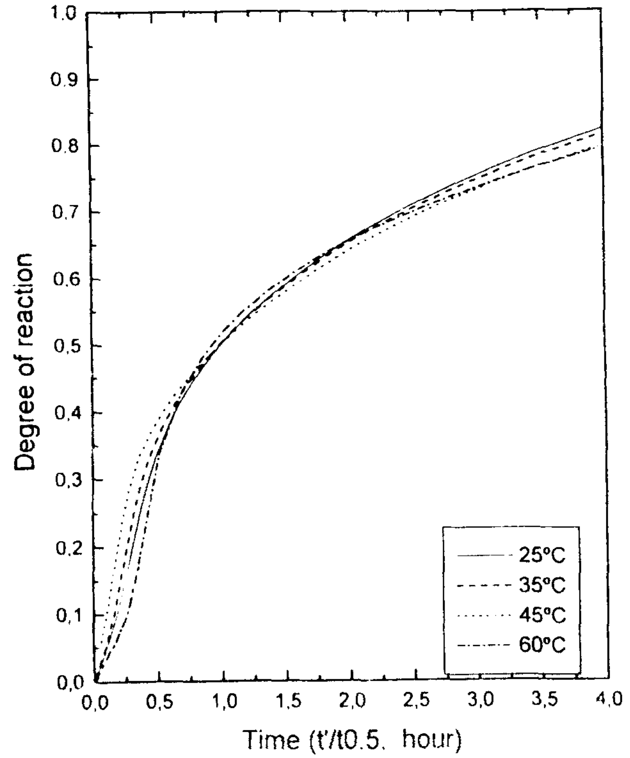

FIG. 4.
Degree of reaction vs. $t'/t'_{20.5}$.

Jander equation:

$$D_3 = (1 - (1 - \alpha)^{1/3})^2 = (k/r^2)t = 0.0426(t/t_{0.5}) \qquad [5]$$

α = degree of reaction; K = constant; r = radius of particles; $t_{0.5}$ = time necessary for $\alpha = 0.5$. Ginstling-Brounshtein equation:

$$D_4 = (1 - 2\alpha/3) - (1 - \alpha)^{2/3} = (k/r^2)t = 0.0367(t/t_{0.5}) \qquad [6]$$

Jander equation [5] fits better experimental data. Slope values obtained when this equation is applied are given in Table 4.

Both equations [5] and [6] explain the diffusion process considering the relation between the total initial volume of particles that have reacted and the initial volume of particles. According to Ginstling and Brounshtein (15), Jander equation is valid when the ratio between the width of the hydration products layer (x) and the radius of the initial particles (R) is less than 0.5, which involves a low conversion degree of the initial particles. The Ginstling-Brounshtein equation is better adjusted to processes where this ratio X/R > 0.5, this is, in processes where a high conversion degree of the initial particles has been taken place.

TABLE 4

Slope Values According to Eq. [5]

Slope of diffusion equation	TEMPERATURE (°C)			
	25	35	45	60
A (D_3=A t'/$t'_{20.5}$	0.0498	0.0497	0.0449	0.0440
K' (D_3=K' t')	0.0063	0.0149	0.0247	0.0755

In the definite case of the alkaline activated slag and at the studied ages, the degrees of reaction were low. This was verified by the method of methanol-salicylic acid (11), remaining a high proportion of anhydrous slag unreacted. The system is in a situation close to that explained by Jander equation.

2. Activation Energy. Applying $D_3(\alpha)$ = K't' equation [5], rate constants (K' = K/r^2) were determined at the different temperatures. The values obtained are collected in Table 4. Applying Arrhenius equation [7], activation energy of the slag from the induction period was determined.

$$K = K_0 \exp(-AE^a/RT) \qquad [7]$$

In Fig. 5, Ln K' vs. 1/T (°K) is represented. From the straight slope, activation energy of the process was determined. This value is 57.6 KJ/mol.

AE^a value obtained after the induction period for a blast furnace slag, activated with Na_2SiO_3 + NaOH at 4%Na_2O is the same order of that obtained by Wu et al. (16) for a cement with slag containing 50% of slag (49.1 KJ/mol); Regourd et al. (17) for a cement with slag with a 80%

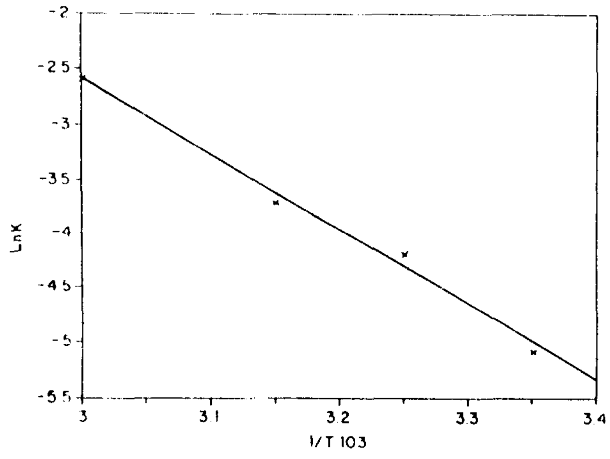

FIG. 5.
Activation energy.

of slag (50 KJ/mol) and by Huanhai et al. (8) for slag activated with water glass of SiO_2/Na_2O = 1 (the apparent activation energy was 53.63 KJ/mol).

Conclusions

The most relevant conclusions extracted from the present study are the following:

1. Through different methods it has been determined that, after the induction period, diffusion is the mechanism controlling alkaline activation slag process (specifically when the activator was a mix of $Na_2SiO_3/NaOH$ with a total concentration of 4% Na_2O wt.).
2. Jander equation ($D_3 = (1 - (1 - \alpha)^{1/3})^2 = (k/r^2)t = 0.0426\ (t/t_{0.5})$) fits better to experimental data and it is the best explaining the values obtained.
3. Activation energy (AE^a) for the process was determined. These value is 57.6 KJ/mol.

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