Pergamon

Cement and Concrete Research, Vol. 27, No. 1, pp. 63-73, 1997

0008-8846/97 $17.00 + .00

PII S0008-8846(96)00195-0

STUDY OF THE REACTIVITY OF CLINKERS BY MEANS OF THE CONDUCTOMETRIC TEST

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(Refereed)
(Received July 10, 1996, in final form November 19, 1996)

ABSTRACT

The conductometric test has been developed by Vernet in order to study cement-admixture systems. An investigation has been carried out to see how this test can be used to control the reactivity of clinkers.

Six cements provided by the same plant were studied. The conductometric test showed different behaviours, in terms of initial and maximal conductivity values and duration of the dormant period. These results, completed by the analyses of the pore solutions, explained the different 2-day and 7-day compressive strengths.

The conductometric test could be an interesting way to follow the reactivity of cement. *Copyright © 1997 Elsevier Science Ltd*

Introduction

Cement is one of the main components of concrete, and the quality of concrete depends to a great extent on its quality (also on that of aggregates and admixtures). The quality of cement, representated by its strength development, is the integrated result of proportioning and processing of the raw materials for the kiln feed, the burning process in the kiln and the subsequent cooling, and the grinding process of cement clinker. The quality of cement is controlled by each cement manufacturer according to a set of national standards: mortar strength development, setting time, etc... Usually, the strength of a cement is considered as the most important of its properties. Strength may vary for several reasons, reported in (1).

In this paper, six samples of cement are investigated; they were provided by the same plant and gave different strengths. The conductometric test, developed by Vernet (2), was used to understand the reasons of these variations.

Experimental

Materials. Six Ordinary Portland Cements provided by the same plant are studied. Chemical analyses of each clinker are given in Table 1. Each sample of clinker was taken every two days.

TABLE 1 : Chemical Analyses of Clinkers. Properties of Cements

	C1	C2	C3	C4	C5	C6
Chemical Analyses : percentage (by weight)						
L. on I.	0.23	0.29	0.20	0.27	0.32	0.22
Free CaO	0.78	1.18	0.78	4.48	1.41	2.90
SiO_2	21.44	21.08	21.38	21.06	20.64	21.38
Al_2O_3	5.37	5.35	5.46	5.49	5.41	5.37
Fe_2O_3	3.70	3.63	3.65	3.69	3.74	3.62
CaO	66.63	66.37	66.04	66.15	66.60	66.85
MgO	0.72	0.67	0.68	0.68	0.67	0.67
K_2O	0.61	0.74	0.90	0.87	0.88	0.92
SO_3	0.21	0.30	0.43	0.47	0.41	0.58
TiO_2	0.35	0.33	0.34	0.38	0.35	0.36
MnO	0.08	0.07	0.07	0.07	0.07	0.07
P_2O_5	0.28	0.31	0.31	0.28	0.29	0.29
Bogue Composition						
C_4AF	11.3	11.0	11.1	11.2	11.4	11.0
C_3A	8.0	8.0	8.3	8.3	8.0	8.1
C_3S	63.7	64.0	61.2	48.8	66.8	53.2
C_2S	13.5	12.2	15.2	23.7	8.9	21.0
Blaine Surface (m^2/kg)						
	301	318	308	305	308	318

Figure 1 show the 2-day and 7-day compressive strengths obtained for each cement.

C1, C4 and C6 lead to the lower strengths (<25MPa) at two days, while C2 and C5 give the better one (>28 MPa). At seven days, only C4 and C6 give slight strengths (<42 MPa). C1 leads to better result: 45 MPa, while C2, C3 and C5 give more than 46.5 MPa.

Conductometric Test

Conductivity of solutions. Principle. The conductivity of a solution is measured by applying an alternative voltage between two electrodes in a conductivity cell. At any instant in time,

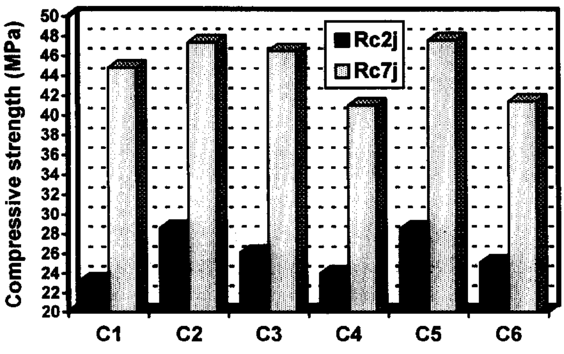

FIG. 1.
2-day and 7-day compressive strengths.

anions migrate towards the positive electrode and cations towards the negative one. The conductivity of the solution (in S/cm) is the conductance which would be measured in a standard cell containing two electrodes of $1 cm^2$ surface area held 1 cm apart.

The conductivity of a dilute solution is the sum of the individual contributions to conductivity of all the ions in the solution multiplied by their concentration : conductivity is directly proportional to concentration. This is called Kohlraush's law of independent migration. It states that each ion carries its portion of the total conductivity without being affected by any of the other ions in solution. Stated as an equation :

$$\kappa = \frac{\sum \lambda^\circ_i c_i}{1000}$$

where κ is the measured conductivity in S/cm

C_i is the concentration of the ions in equivalents/l

λ°_i is the ionic limiting equivalent conductivity, specific for each ion. Table 2 lists λ°_i for some inorganic ions.

Apparatus. This test has been developed by Vernet (2) in order to study cement-admixture systems. The measuring device, called "conductometric multiplexer" allows the simultaneous monitoring of 9 suspensions. Cells are kept in a temperature regulated box.

Vernet analysed the conductometric signal and the different causes of its variation and defined the most pertinent experimental conditions with respect to the aims of the tests (evaluation of the chemical secondary effects of admixtures). He was lead to work on suspensions with a water-cement ratio of 4, for which the causes of variations of conductivity can be neglected.

Such method has been used on cement pastes by other researchers, in order to characterize the behaviour of cement during setting (3 to 6).

Variations of the electrical conductivity during cement hydration. Figure 2 shows the variations of conductivity of a concentrated suspension of OPC hydrated at a water-cement ratio of 4.

During the mixing period (I) :

Dissolution rate of clinker components and gypsum is high. The ions passing into solution increase instantaneously the conductivity. After a few minutes, the solution becomes supersaturated with respect to ettringite and C-S-H. Precipitation of C-S-H begins.

TABLE 2

Equivalent Conductivities in Aqueous Solution at 25°C ($S*cm^2$/equiv.)

Anions	λ°_i	Cations	λ°_i
OH^-	198	H^+	350
Cl^-	76	Na^+	50
SO_4^{2-}	80	K^+	74
		Ca^{2+}	60

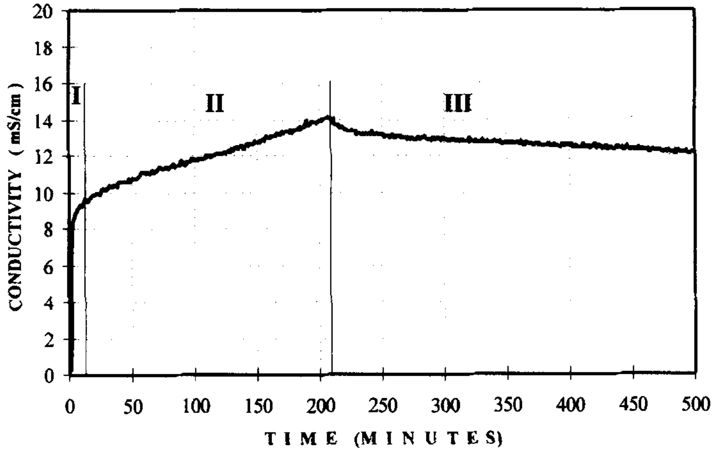

FIG. 2.
Evolution of the electrical conductivity of a suspension of OPC (water-cement ratio = 4).

During the dormant period (II) :

The reactions continue slowly, forming ettringite and C-S-H. The solution becomes richer in calcium, because only half of the calcium of C_3S is used to make C-S-H. The other part goes into the solution (in Ca^{2+} and OH^- ions form). Because of the slow nucleation mechanism of portlandite, the solution becomes supersaturated with respect to this hydrate, what causes the increase in conductivity. From a critical level of supersaturation, the portlandite begins its precipitation, that gives a sudden decrease of conductivity, after reaching a maximum. This moment is defined as the end of the dormant period.

During the acceleration (III) :

Reactions are accelerated, due to portlandite precipitation, the total dissolved ions being now consumed by precipitation. This period begins with a slow decrease of the conductivity.

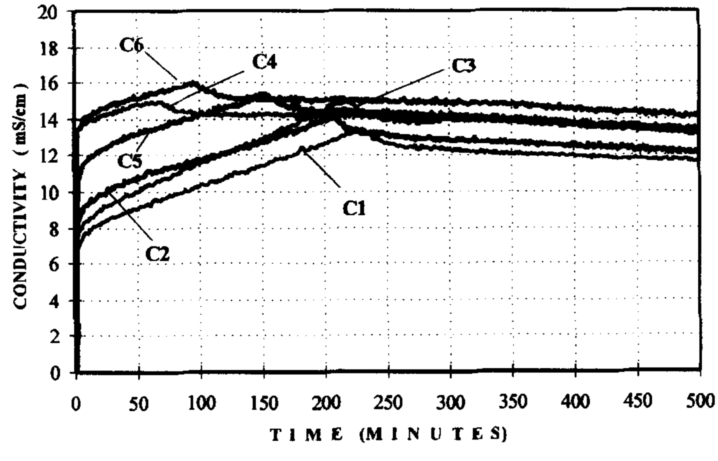

FIG. 3.
Evolution of the conductivity of the OPC suspensions (W/C = 4).

TABLE 3

Results Obtained with the Conductometric Test

Cement	Initial conductivity (mS/cm)	Maximal conductivity (mS/cm)	Duration of the dormant period (min.)
C1	6.8	13.4	230
C2	8.3	14.1	205
C3	7.7	15.0	215
C4	13.2	15.0	75
C5	10.6	15.4	150
C6	13.5	16.0	95

Results

Suspensions of cement were prepared with 70 ml of deionized water and 17.5 g of cement (W/C = 4). The evolution of conductivity of these suspensions is shown in Figure 3. Table 3 presents values of initial conductivity, measured 2 minutes after the introduction of cement in water, maximal conductivity and duration of the dormant period. These results are obtained with an error of 2% for conductivity values and a reproductibility of 10 minutes for the duration of dormant period.

Cements C1, C4 and C6, which give slight compressive strengths are characterized by:

- slight values of initial and maximal conductivities for C1
- a high value of initial conductivity and a short dormant period for C4 and C6.

The conductometric test shows different behaviours, but this global measurement can not explain the reasons of such results.

Analysis of Solutions. In order to understand results of conductometry, suspensions of cement were filtered two minutes after the introduction of water. Analysis of the recovered solutions were carried out as follows. Concentrations of K^{+}, Na^{+}, Ca^{2+} and SO_4^{2-} were determined by ion chromatography; OH^{-} concentrations were determined by titration against standard HCl (0.1N).

Results are shown in Figures 4a to 4e. C4 gives the highest calcium ion content, while C3 and C5 give the lowest ones. C4 and C6 lead to high hydroxyl ion contents. C1 gives low potassium ion concentrations, while C4 and C6 give high sodium ion contents. All the cements give the same sulphate ion content.

Remarks about conductivity of suspensions. Figure 5 shows the approximative contribution of each ion to the total conductivity despite the Kohlraush's law can only be applied to dilute solutions. As concentration increases, the direct proportionality between conductivity and concentration is lost. In our case, the principal contribution (60 to 80%) comes from the hydroxyl ion concentration: OH^{-} content is high for each cement, and the OH^{-} equivalent conductivity $\lambda°$ is the highest one: 198. Table 4 compares measured and calculated conductivity values after two minutes of stirring. Measured conductivity is always lower (from 3 to 25%) than the calculated one, but trends are kept.

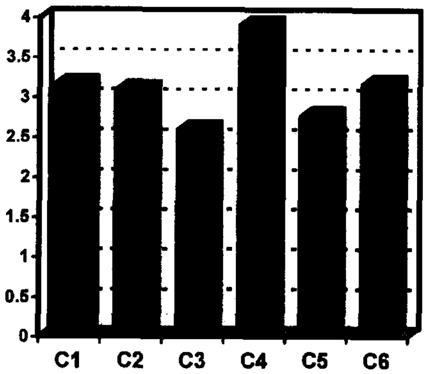

FIG. 4a.
Calcium Ions (*10^{-2} mol/l).

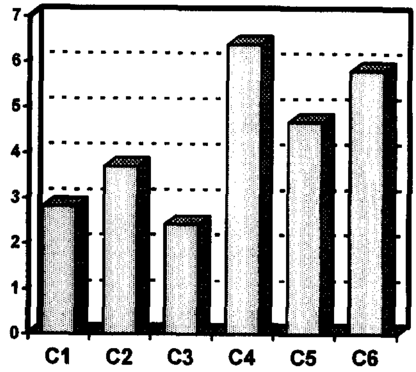

FIG. 4b.
Hydroxyl Ions (*10^{-2} mol/l).

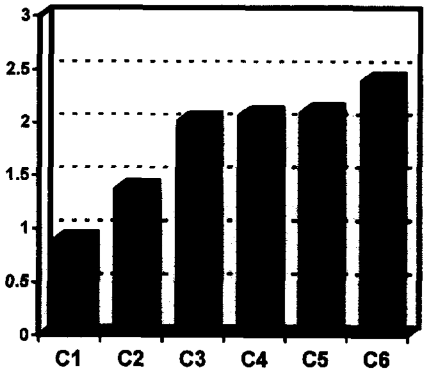

FIG. 4c.
Potassium Ions (*10^{-2} mol/l).

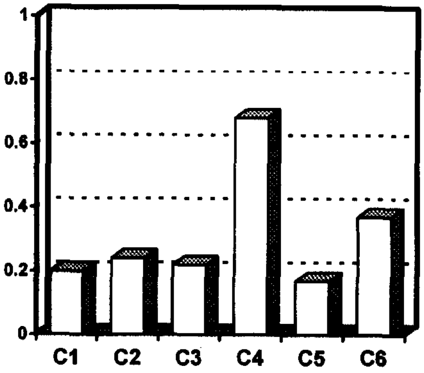

FIG. 4d.
Sodium Ions (*10^{-2} mol/l).

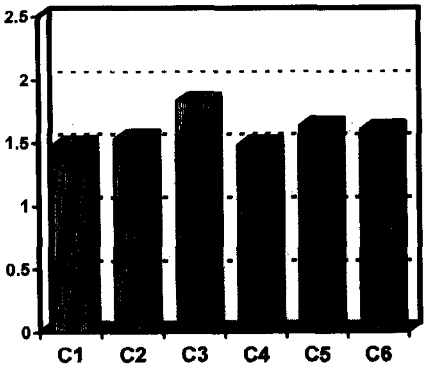

FIG. 4e.
Sulphate Ions (*10^{-2} mol/l).

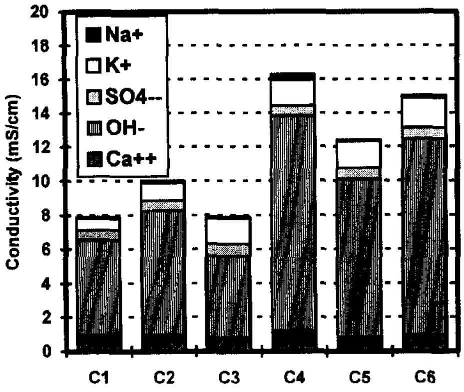

FIG. 5.
Contribution of each ion to the total conductivity.

C1 presents a deficience in soluble potassium content. Chemical analysis shows lowest values of K_2O and SO_3 for this cement. According to Osbaeck (7), it is possible to compute the soluble alkalis from the clinker composition (Figure 6).

Values of Ks (total soluble potassium) of cements C1 to C6 are given in Table 5.

These results show that the amount of soluble alkalis vary from 40 to 64% of the total alkali content. McCoy (8) has reported that it could vary between less than 10% to over 60%. Figure 7 shows that there is a very good correlation between Ks and $[K^+]$ measured 2 minutes after the beginning of the hydration.

The alkalis are introduced to the raw mixture for the OPC clinker mainly as a component of clayey minerals and, in some amount, with coal and electrofilter dust, if it is fed back to the rotary kiln. The alkalis react at first with sulphur forming sodium and potassium sulphates (9). In the absence of SO_3, alkali oxides are incorporated into the crystalline lattice of clinker minerals while, in the presence of SO_3, alkali sulphates (designed also as " soluble alkalis ") are formed (10). The action of alkalis depends to a great extent on the form in which they are present in clinker. From numerous data it results that the soluble alkali content increase leads to an increase of early strength and a decrease of late strength values (11, 12, 13 and 14).

The slight 2-day strength of C1 is explained by its deficience in soluble potassium content, which also explains the better strength gain between 2 and 7 days for this cement. This deficience leads to a slight initial conductivity value and may be to a longer duration of the dormant period.

Odler and Wonnemann (15) reported a decrease of both early and late strengths due to Na_2SO_4 in cements. C4 and C6 present the highest soluble sodium content that could explain

TABLE 4

Comparison Between Measured and Calculated Conductivity Values (mS/cm)

	C1	C2	C3	C4	C5	C6
Measures	6.8	8.3	7.7	13.2	10.6	13.5
Calculated Values	7.9	10.0	7.9	16.3	12.4	15.0

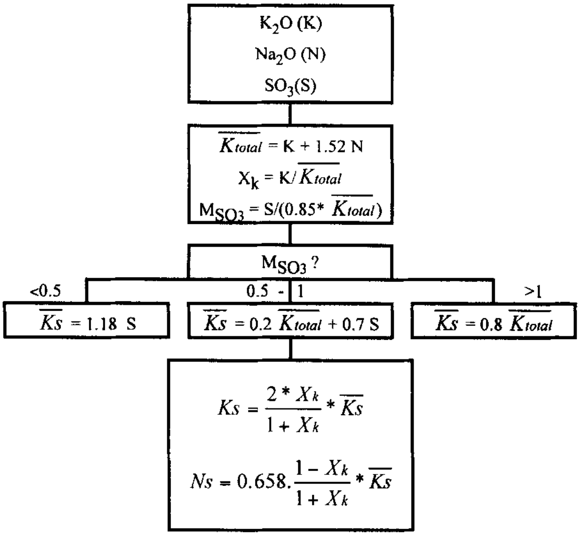

FIG. 6.
Calculation of the soluble alkalis (7).

the slight strengths obtained at 2 and 7 days. But these two cements give also high Ca^{2+} contents and C4 has a high hydroxyl ion concentration.

The microscopic observations were carried out using a SEM (JEOL 840) equipped with an EDS detector (Tracor).

Figure 8 shows a lot of calcium hydroxide crystals, which look like cauliflower, called epezite and surrounding the original particle of free lime (16, 17). Epezite is forming via air slaking: if burning or cooling are unsatisfactory, the excess lime will remain in a free condition. This hard-burnt lime hydrates only very slowly and, because slaked lime occupies a larger volume than the original free calcium oxide, expansion takes place, which can lead to clinker disintegration (18). This excess free lime explains the high initial conductivity and the short dormant period. It also gives a deficience in C_3S, as shown in Table 1.

Osbaeck (7) has established a correlation between the amounts of C_3S (according to Bogue) and total soluble alkalis $\overline{Ks}$ and the mortar compressive strength at 28 days, in order to estimate changes in strength development for varying clinker compositions :

$$\sigma = 51.9 - 10.3\overline{Ks} + 0.15C_3S \qquad \text{(MPa)}$$

Results are shown in Figure 9.

These results are in good agreement with literature:

TABLE 5

Calculation of Total Soluble Potassium in K_2O Equivalents, According to (7).

	C1	C2	C3	C4	C5	C6
K_2O	0.61	0.71	0.90	0.87	0.88	0.92
SO_3	0.21	0.30	0.43	0.47	0.41	0.58
Ks	**0.24**	**0.35**	**0.48**	**0.50**	**0.46**	**0.59**
Ks/K_2O	40%	49%	53%	57%	52%	64%

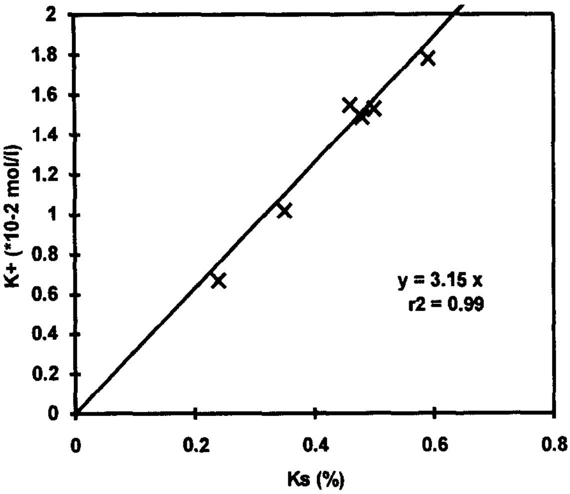

FIG. 7.
Correlation between Ks and [K+].

* the deficience of soluble alkalis content of C1 leads to a decrease of early strength and an increase of late strength values.

* because of the deficience of C_3S due to the excess of free lime, strengths of C4 and C6 stay low.

Conclusion

An investigation has been carried out to examine the possible contribution of the conductometric test to control the reactivity of cement.

The following conclusions have been drawn from the results of this paper :

- a low initial conductivity (measured two minutes after the blending of cement with water) is explained by a deficience of soluble alkalis, leading to slight initial strength of mortar, but without effects on late strength

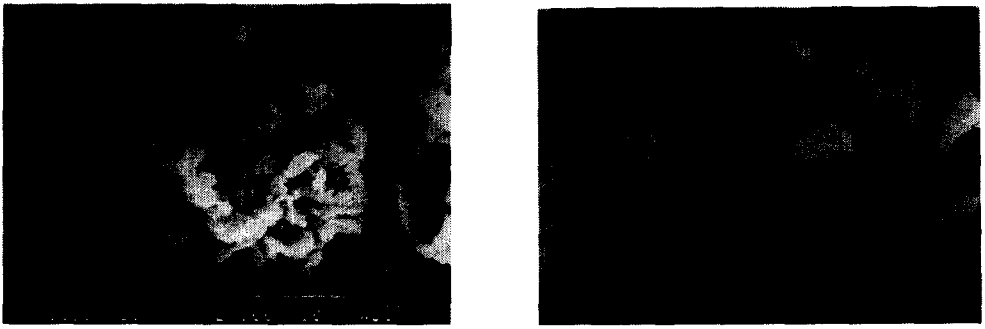

FIG. 8.
SEM micrographs: Epezite crystals.

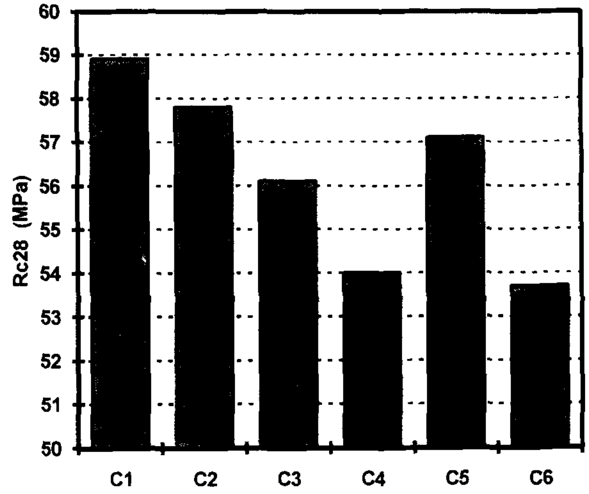

FIG. 9.
Calculation of the mortar compressive strength at 28 days (7).

- high initial conductivity and short dormant period have been explained by the presence of hard-burnt free lime, called epezite, and leading to low strength.

In conclusion, this simple test could be used to follow the reactivity of cement.

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