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INFLUENCE OF THE MINERALOGICAL COMPOSITION, SPECIFIC SURFACE AREA AND STRAINS - CRYSTALLITE SIZE OF ALITE ON THE COMPRESSIVE MECHANICAL STRENGTH OF PORTLAND MORTARS. II. CLINKERS OF HIGH TRICALCIUM ALUMINATE CONTENTS

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ABSTRACT

Multiple linear regression and factor analysis have been used to investigate the influence of the clinker features (mineralogical composition, specific surface area, strains-crystallite size of alite and crystallite size of C_3A) on the 1, 3, 7 and 28-day compressive mechanical strength of a series of Portland cement mortars of very high C_3A contents. A mathematical model based on the linear weights of the considered variables that might be of help to understanding the complex hydrolysis of minerals in Portland cement has been employed. A large set of clinkers from "Portland de Mallorca" where alite, belite and tricalcium aluminate occur essentially in their rombohedral, beta and cubic forms, respectively, and the ferrite phase occurs in its rhombic form has been chosen. We performed hourly samplings in order to obtain a daily average clinker.

Introduction

In the last few years various mathematical models have been used to estimate the mortar mechanical strength from some clinker characteristics. As we have mentioned in Part I [1] while some authors [2] believe that the mineralogical composition accounts by itself for the variability of the mechanical strength at given mortar ages, others [3,4] have pointed out that decreased grain size ranges result in increased compressive strength as a result oh the higher cristallinity of the resulting hydrates.

Taylor [5] assumed the hydrates to preserve a "memory" of the initial assembly of grains in the cement. Luna [6] found no correlation between the decrease in strength observed after 14 days or longer and the degree of free lime saturation, gypsum content, fineness or C_3A content, so he concluded that the aforementioned decrease arose from the intrinsic nature of the hydration process.

Popovics [7] hypothesized that the hydrolysis of alite and belite takes place by a first-order mechanism in which C_3A acts as a catalyst. Some authors [8] account for the hydraulic activity of the different phases on the basis of the different surface density of Brönsted acid sites and some others [9] believe that the primary process involved in the hydration is the partial protonation of unsaturated oxide ions, which favours the hydrolysis of alite over that of β-belite.

To our minds, the role of each observable (phase proportions, microstructural parameters, specific surface area, reaction medium, *etc.*) in determining the strength of mortars at different ages remains to be clarified.

As we have mentioned in Part I, if the rate of change of the strength is assumed to be roughly similar to that of hydrolysis, then the change in the strength arising from hydrolysis of a given phase can be expressed as

$$dS/dt = P.K.f(\alpha)$$

where P is the percent weight of a given hydraulic product, $K(T) = A \exp(-E/RT)$ the Arrhenius rate constant, T the absolute temperature, A the pre-exponential factor, E the activation energy of the process, and $f(\alpha)$ a function dependent on the hydrolysis mechanism of the product concerned, α being the hydrated fraction.

As a rule, both the rate constant and $f(\alpha)$ can be different for each of the hydraulic products and depend on such physico-chemical features as the grain size distribution, specific surface area, crystal size, strains, *etc.* Any phase or foreign ion, whether internal or external, configures a local atmosphere that can also alter the thermodynamics and kinetics of hydrolysis, especially in its first stadiums [10-12]. The relative hydrolysis rate of the different phases might determine the mutual steric hindrance of the products [13,14]. All these variable effects, asociated to the $K(T)f(\alpha)$, change for each phase. However, as there exists an interdependence among the phases it is imposible to obtain the total change in strength by addition of the particular change corresponding to each independent phase. With this in mind, in this work we have used various statistical methods to assess the relative significance of the $K(T)f(\alpha)$ product to some characteristic variables of the clinkers such as their composition, grain fineness and, especially, the degree of crystallinity of alite (crystallite size and strains) and crystallite size of C_3A. For this purpose we have taken into account the values of the aforementioned variables and those of compressive mechanical strength at 1, 3, 7 and 28 days.

Materials and methods

Materials

We have studied 29 industrial samples that were the daily averages of hourly clinkers. The XRD diagram of the marl employed (from Lloseta, Baleares, Spain) shows quartz, calcite, dolomite, feldspat, illite and kaolinite as principal components.

Theoretical and experimental methods

Specific surface areas were measured by using a Blaine permeabilimeter. The potential mineralogical compositions were determined from the results of the chemical analyses by using Bogue's formulae. The crystallite size and strains were obtained by applying the variance procedure to the X-ray diffraction peak corresponding to plane (021) of alite and (008) of the C_3A. The statistical analysis was performed with the aid of the multiple linear regression programme P1R and the factor analysis was carried out with the program P4M of the BMDP.

Results and discussion

Table 1 gives the average chemical composition of the clinkers set. Table 2 gives the clinker average potential mineralogical composition. Table 3 shows the average values of the crystallite size and strains of alite, crystallite size of C_3A and specific surface of the clinker set. Figure 1 shows the average compressive strength of the standardized mortar as a function of its age.

TABLE 1
Average chemical analysis of the clinker set.

SiO_2	21.15 ± 0.21
Al_2O_3	0.01 ± 0.20
Fe_2O_3	2.64 ± 0.07
CaO	66.63 ± 0.20
K_2O	0.78 ± 0.10
SO_3	1.29 ± 0.14

TABLE 2
Average potential mineralogical composition of the clinker set.

C_3S	58.10 ± 0.26
C_2S	16.73 ± 0.23
C_3A	11.41 ± 0.56
C_4AF	8.00 ± 0.23
CaO free	1.10 ± 0.26

TABLE 3
Average crystallite size and strains of the alite, crystallite size of C_3A and specific surface of the clinker set.

C_3S Tv(021), A	279 ± 34
C_3S Mv(021) x 10^6	1932 ± 300
C_3A Ts(008), A	304 ± 13
Blaine, cm^2/g	4411 ± 419

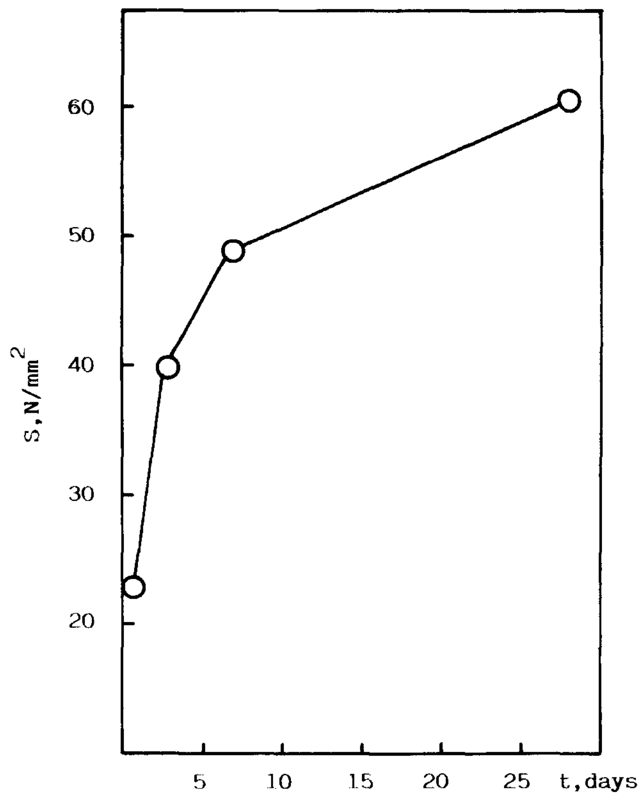

FIG.1
Compressive mortar strength as a function of the age.

Multiple regression analysis

In performing this type of statistical study, which is fairly easy to interpret in mathematical terms, we have considered the K_2O, SO_3, C_3S, C_2S, C_3A, C_4AF, free CaO contents and specific surface as well as strains and crystallite size relative to plane (021) of alite so as the crystallite size relative to plane (008) of C_3A to be the independent variables, and the compressive strength at different ages the dependent variable. Regression coefficients, listed in Table 4, seem not to have a physical significance but the mathematical fitting is quite good.

Our greatest interest is centered in the determination of the real "weight" or degree of linear coverage (physical significance) of each selected independent variable on the strengths. This made it advisable to perform a prior factor analysis, which is carried out as described below:

Factor analysis

As we said in Part I, in factor analysis, the variance of each observable is assigned to a unity vector with a given direction whose projection on each factor —the different factors can be

TABLE 4

Linear regression and multiple correlation coefficients obtained by multiple linear regression between the mortar compressive strength and the rest of the variables shown below.

	One day	3 days	7 days	28 days
Intercept	-10.95	1987.37	367.46	777.94
K_2O	-60.89	-52.37	-4.55	-13.40
SO_3	102.89	101.40	137.19	50.41
C_3S	-8.18	-26.43	-10.33	-0.54
C_25	-13.55	-33.02	-16.62	-5.75
C_3A	0.25	-14.55	5.23	4.67
C_4AF	27.74	-26.95	24.25	-0.52
CaO	-8.75	-45.78	-47.07	-12.20
Blaine	0.03	0.04	0.03	0.03
C_3S strain	84504.43	155786.80	102325.60	-62953.11
C_3S cryst. size	0.99	1.30	0.50	-0.70
C_3A cryst. size	0.19	-0.01	0.19	0.07
R-SQ(adj.)	0.5498	0.5822	0.6361	0.4962

considered to be linearly unrelated space directions— provides the percentage of the variable that is linearly related to the factor. Likewise, observables falling on the same factor will be linearly correlated, so the apparent linear weight of one variable over another will be given by the factor-extended sum of the products of the corresponding factor coefficients.

Tables 5-8 list the factor coefficients of the samples. Ideally, the communalities corresponding to the strengths should have been close to unity, so their variability would have been fully accounted for by the considered observables. This has not been the case: part of the variability of strengths probably arose from other observables (small impurities, homogeneity differences, *etc.*) not included in the set which might alter the activity of all or

TABLE 5

Results of the factor analysis. Mortar age = 1 day.

Observables	Communality	Factor 1	Factor 2	Factor 3	Factor 4
Strength	0.726	0.836	0.047	-0.232	-0.118
K_2O	0.418	-0.147	0.281	-0.406	0.738
SO_3	0.816	0.578	-0.311	-0.475	-0.311
C_3S	0.996	0.582	0.670	0.416	0.030
C_2S	0.995	-0.567	-0.703	-0.292	-0.032
C_3A	0.904	-0.505	-0.371	0.085	-0.028
C_4AF	0.628	-0.186	0.595	-0.402	0.224
CaO	0.800	-0.213	-0.095	-0.731	0.065
Blaine	0.520	0.665	0.050	-0.392	0.037
C_3S strain	0.982	-0.723	0.527	-0.047	-0.251
C_3S cryst. size	0.982	0.734	-0.500	0.069	0.269
C_3A cryst. size	0.450	-0.023	-0.462	0.488	0.463
% variance expl.		29.7	19.8	15.1	8.9

TABLE 6

Results of the factor analysis. Mortar age = 3 days.

Observables	Communality	Factor 1	Factor 2	Factor 3	Factor 4
Strength	0.746	0.811	0.119	-0.192	-0.286
K_2O	0.405	-0.144	0.294	-0.388	0.675
SO_3	0.812	0.562	-0.329	-0.518	-0.314
C_3S	0.996	0.643	0.607	0.415	0.083
C_2S	0.995	-0.624	-0.646	-0.295	-0.089
C_3A	0.906	-0.528	-0.323	0.100	-0.101
C_4AF	0.625	-0.198	0.612	-0.347	0.275
CaO	0.811	-0.258	-0.064	-0.720	0.146
Blaine	0.556	0.666	0.016	-0.420	0.010
C_3S strain	0.983	-0.653	0.594	-0.022	-0.333
C_3S cryst. size	0.983	0.667	-0.569	0.045	0.347
C_3A cryst. size	0.445	-0.057	-0.478	0.485	0.361
% Variance expl.		29.2	19.9	14.9	9.4

some of the products contributing to the compressive mechanical strength.

Figure 2 shows the variation of the apparent linear weights (A_{LW}) on the strengths of the studied observables as a function of the age of the standardized mortars: The K_2O seems to have only some small negative influence on the strength. The SO_3 shows a high positive effect; the SO_3/K_2O relation is, in addition, close to the ideal, equal to 1.5 [15]. The C_2S has an adverse effect at any age. The C_3A shows a negative influence at any age too; this could be justified by considering that the product of its hydrolysis is poorly crystallized [16]; some authors [17] find that C_3A shows a positive effect only after times greater than 28 days. The C_4AF and free CaO don´t seem to have only a very weak influence on the strength. The apparent linear weight of C_3S is positive in the whole range. The specific surface presents the more important

TABLE 7

Results of the factor analysis. Mortar age = 7 days.

Observables	Communality	Factor 1	Factor 2	Factor 3	Factor 4
Strength	0.779	0.766	0.188	0.206	-0.281
K_2O	0.382	-0.099	0.317	0.400	0.638
SO_3	0.837	0.547	-0.336	0.535	-0.378
C_3S	0.996	0.671	0.550	-0.436	0.103
C_2S	0.995	-0.656	-0.595	0.316	-0.109
C_3A	0.905	-0.530	-0.278	-0.079	-0.120
C_4AF	0.628	-0.127	0.641	0.351	0.221
CaO	0.817	-0.293	-0.048	0.697	0.232
Blaine	0.551	0.666	-0.005	0.425	-0.028
C_3S strain	0.982	-0.626	0.638	-0.001	-0.419
C_3S cryst. size	0.982	0.641	-0.614	-0.023	0.345
C_3A cryst. size	0.451	-0.060	-0.480	-0.453	0.418
% Variance expl.		28.5	20.1	14.9	9.1

TABLE 8

Results of the factor analysis. Mortar age = 28 days.

Observables	Cammunality	Factor 1	Factar 2	Factor 3	Factor 4
Strength	0.694	0.750	0.230	-0.182	-0.307
K_2O	0.385	-0.110	0.314	-0.385	0.655
SO_3	0.804	0-497	-0.359	-0-527	-0.324
C_3S	0.996	0.704	0.516	0.427	0.110
C_2S	0.995	-0.683	-0.561	-0.312	-0.131
C_3A	0.905	-0.559	-0.256	0.101	-0.078
C_4AF	0.614	-0.138	0.633	-0.323	0.300
CaO	0.801	-0.270	-0.021	-0.719	0.160
Blaine	0.626	0.688	-0.013	-0.449	-0.097
C_3S strain	0.982	-0.592	0.673	0.013	-0.341
C_3S cryst. size	0.982	0.602	-0.652	0.014	0.365
C_3A Cryst. size	0.446	-0.068	-0.477	0.447	0.255
% Variance expl.		28.2	20.3	14.8	9.2

positive effect, which is easily justified by considering that the reactivity increases as the particles become smaller.

Strains of the alite have an adverse effect on the strength in every case. In fact, even if the increasing lattice defect contents result in increasing hydrolysis rates, as does the higher specific surface corresponding to smaller particle sizes, it does not necessarily imply a greater contribution to compressive mechanical strength since the hydrolysis products might keep an appreciable "memory" of the defect content of the driving solid [18]. On the other hand, the crystallite size of alite seems to have a positive effect on the mechanical strength of the mortars that diminishes susbtantially with age.

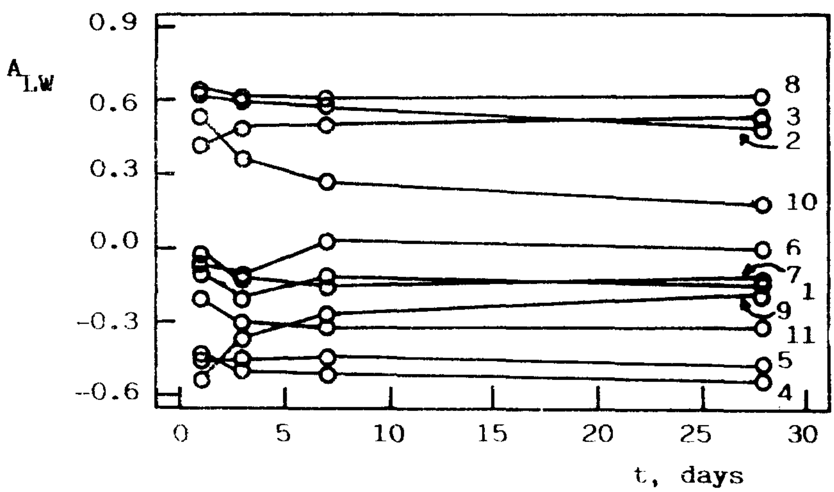

FIG.2

Variation of the apparent linear weight of the variables as a function of mortar age. 1=K_2O, 2=SO_3, 3=C_3S, 4=C_2S, 5=C_3A, 6=C_4AF, 7=Free CaO, 8=Blaine, 9=C_3S strain, 10=C_3S cryst. size, 11=C_3A cryst. size.

Conclusions

The factor analysis allows us to establish a generic relation between strengths and standardized independent variables of the form

$$R = \%SO_3xP_1 + \%C_3SxP_2 + \%C_2SxP_3 + ... + \text{intercept}$$

where P_1, P_2, *etc.* denote the linear weights on the strengths of the corresponding independent variables, which vary with the mortar age and, less markedly, with the type of clinker. This equation is easy to interpret in physical terms and is more general than the regression hyperplane obtained by applying multiple linear regression. This latter is highly sensitive to the elimination or addition of a new independent variable, which results in the variation of all the regression coefficients —usually devoid of physical significance— that define the hyperplane.

On the other hand, the communality, which is a clear expression of the linear coverage of the other observables on the strengths, allows one to determine whether the selected set is adequate or, more commonly, requires expansion by including other observables not previously considered.

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