Kinetics of Cement Strength Development Using Different Types of Cement and Aggregates

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Abstract: - The object of the present study is the kinetics of cement strength development using different cement and aggregate types. The model that has been developed uses the following data: (1) Composition of cement. (2) Mineral composition of clinker. (3) Cement fineness. (4) Early, standard and long-term strength data. (5) Aggregates nature. The parameters of the model are constituted by: (1) The hydration rates of the mineral phases of clinker that are a function of the cement fineness. (2) The contribution of each phase to the cement strength. As far as the hydration of phases is concerned first order kinetic has been used. The parameters of the model were calculated through fitting to experimental points of strength for the cement types CEM I and CEM II A-L produced in the factory of HALYPS. Siliceous and calcareous aggregates were utilized. The effect of the clay, sometimes existing in the concrete aggregates is also investigated and incorporated in the mathematical treatment. . The impact of the aggregates type on the mortar strength development and variance is linked with physical characteristics of the aggregates. The mathematical model can be utilized for the cement composition design, as well as a quality control tool for regulation of the current production

Key-Words: - Strength**,** Hydration, Kinetics, Cement, Aggregates, Clinker, Model

1 Introduction

The development of cement strength as a consequence of the clinker characteristics and of the physical and chemical properties of the cement constitutes one of the most critical issues in the field of the cement type design and its quality control. Obviously, the development mentioned is strictly connected with the hydration of the mineral phases of the clinker. The hydration of the cement is one of the most important subjects in the international literature [1, 2, 3]. Certain mathematic models about estimation of the hydration degree as a function of the mineral characteristics of the clinker, using several methods of measuring the hydration, have also been developed [4, 5]. Models to predict the compressive strength based on the water to cement ratio [6] and on the Knudsen equation [7] have also been derived. The drawback of this kind of models is that it is not easy to distinguish between the different cement types and clinkers of different activities. The impact also of the type and quality of aggregates used on the strength is not obvious. Moreover, mathematic models have been applied, investigating the correlation between the cement strength and its physical and chemical properties using neural network analysis [8, 9].

In the present study the development of a deterministic kinetic model of estimating the early, standard and long term strengths of the cement is attempted, based on laboratory and industrial data concerning the composition of the clinker and the cement, fineness and strengths for the types CEM I 42.5, CEM I 52.5, CEM II A-L 42.5 produced according to the EN 197-1 standard. Except the standard siliceous sand utilized in the mentioned norm, high purity calcareous sand was tested, of the same particle size distribution as the siliceous one. Then a portion of the fines of calcareous sand were replaced by finely ground clay and the impact on the strength development was examined. In this case the calcareous sand can be characterized as a lower purity aggregate. In the last two cases the cement types CEM I 52.5, CEM II A-L 42.5 have been tested. The specimens curing time has been extended in a period from one day to more than 2000 days in some cases. Once the mathematic model offers results of adequate reliability it can be used as a tool for designing as well as for the current quality control during the production.

2 Experimental

2.1 Tests using standard siliceous sand

The tests were performed using the mentioned three cement types. The CEM I contain only clinker and gypsum as main compounds, while in the CEM A-L, limestone is also included as main constituent. For each type several samples were tested, provided from the Halyps cement plant, in order to have a more realistic picture of the cement variance, belonging to the same type and produced by the same production unit. The cement samples have been taken during the daily routine production in a period of around two years. In this way a population of 55 samples was created. The compressive strength of these cements was measured after a curing of 1 or 2, 7 and 28 days. Some of the samples have been cured for 90 days. The preparation and measurement of the specimens was made according to the standard EN 196-1. Besides the final cement products, intermediate products of the cement mills, such as separator returns and filter products were also utilized. The purpose of this sampling was to enlarge the range of the fineness where the kinetic model would be applicable. By utilizing these three types of products, cement compounds of desired fineness were thus prepared. In this way 7 more specimens of significantly different particle size were constructed. The strength of these samples was measured for times ranging from 1 day to more than 2000 days. A total population consisting of 202 strength results is taken using the described experimental design, so that the results of the model proposed would have the widest field of application possible.

XRF chemical analysis was also performed to each batch of clinker consumed to produce the cements. The free lime – CaO_f – of the clinker is extracted with ethylene glycol and determined with titration using hydrochloric acid. The mineral phases that constitute the potential clinker composition are calculated according the following formulae established by Bogue [10].

$$\text{Alite:}\quad C_3S = 4.07\times\left(CaO - CaO_f\right) - 7.60\times SiO_2 - 6.72\times Al_2O_3 - 1.43\times Fe_2O_3 - 2.85\times SO_3$$

$$\text{Belite:}\quad C_2S = 2.87\times SiO_2 - 0.754\times C_3S \tag{1}$$

$$\text{Aluminate:}\quad C_3A = 2.65\times Al_2O_3 - 1.69\times Fe_2O_3$$

$$\text{Ferrite:}\quad C_4AF = 3.04\times Fe_2O_3$$

SO_3 and loss on ignition (LOI) analysis were also performed in each cement sample according to EN 196-2.

Table 1.Range of the input variables

	Min	Max	Aver.
%Clinker	78.1	95.2	85.8
C_3S	57.4	63.5	60.2
C_2S	14.1	18.0	16.2
C_3A	5.0	8.5	6.7
%R40	2.0	52.5	12.0
Sp (cm^2/gr	1050	4860	3340

The residues at 40 microns, R40, are measured using air jet sieving. The cement specific surface, S_p, was measured according to EN 196-6. For each cement sample its composition as regards the clinker, gypsum and limestone contents was estimated using the method presented in [11]. The minimum, maximum and average values of all the input variables are demonstrated in the Table 1.

2.2 Tests using calcareous sand of high and lower purity

The tests were performed according the following procedure:

(i) Two batches of two cement types were selected: CEM II A-L 42.5 R and CEM I 52.5 N

(ii) Normal strength tests, according to the EN 196-1 norm were performed. Specimens were cured in order to have long term results.

(iii) A large sample of calcareous sand was prepared with the same particle size of the standard siliceous sand. The partial residues to each sieve appear in the table 2.

(iv) Long term strength tests were performed with the same lots of cement, but using calcareous instead of siliceous sand. As regards all the other parameters the norm EN 196-1 was applied.

(v) A part of the fines of the calcareous sand (150 – 75 μ) was substituted with finely ground clay of particle size less than 200 μ

(vi) New mixes of calcareous sand with different clay contents were prepared and strength tests were carried out. The EN 196-1 was applied as to all the remaining parameters – apparatus, times, curing temperatures etc.

Table 2. Particle size of calcareous sand

Size (mm)	Partial residue, %r
2.00	0
1.60	7
1.00	26
0.50	34
0.15	20
0.075	13

Table 3. Chemical analysis of the raw materials

Size	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI
P2-R1.6	0.16	0.04	0.04	52.75	3.56	0.0	0.02	0.0	43.23
P1.6-R1.0	0.18	0.05	0.05	52.86	3.25	0.0	0.02	0.0	42.95
P1.0-R0.5	0.42	0.19	0.13	50.95	4.87	0.0	0.03	0	43.12
P0.5-R0.15	0.26	0.10	0.08	51.47	4.71	0.0	0.02	0	43.10
P015-R0.075	0.44	0.19	0.13	51.05	4.40	0.0	0.05	0.0	43.32
Clay	44.48	11.16	5.30	15.85	2.88	0.04	2.04	0.46	16.04

The chemical analysis of the different limestone fractions as well as of the clay appears in the table 3. As concerns the CEM II A-L 42.5 the following clay content was added to the calcareous sand: 0%, 4%, 8%. The corresponding values for CEM I 52.5 N were 0%, 2% and 4%. The high percentage of clay - up to 8% - was selected in order to investigate the maximum impact of the clay on the mortar strength and workability. The different limestone fractions and clay chemical analysis is shown in the table 3.

The Bogue mineral analysis of the clinker contained in the two cement types tested appears in the table 4. From this table becomes obvious that this clinker has the same characteristics with the clinkers shown in the table 1. The cements fineness also is in the same range of the values shown in the table 1as regards both residue at the 40 microns and specific surface.

Table 4.Cement and clinker analysis

	CEM II A-L 42.5 R	CEM I 52.5 N
%Clinker	82.7	91.2
C_3S	61.9	60.7
C_2S	15.3	16.1
C_3A	7.1	7.1
%R40	11.0	5.0
Sp (cm^2/gr)	3520	3340

3 Model Description

The strength development of the cement results from the hydration of its mineral phases C_3S, C_2S, C_3A. In order to describe the conversion rates of each active phase into a hydrated product, first order kinetics, given by equation (2), were used:

$$\frac{dY\_Hydr(t)}{dt} = F_0 \cdot k\_Y \cdot \left(Y_{Init} - Y\_Hydr(t)\right) \qquad (2)$$

Where Y_Hydr(t) = C_3S_Hydt(t) or C_2S_Hydt(t) or C_3A_Hydt(t), the hydrated part of the corresponding phase of the clinker, Y_{Init} = C_3S or C_2S or C_3A the initial non-hydrated phase, calculated through the Bogue formulae, k_Y = k_ C_3S or k_ C_2S or k_ C_3A the specific rate of hydration for each phase and t =time, measured in days. The factor F_0 is defined as the type factor of the aggregates. The F_0=1 is attributed to the standard siliceous sand. For F0 ≠ 1 – value that shall be estimated via regression analysis – the aggregates are considered as pure calcareous with negligible argillaceous impurities, having the same particle size as the standard siliceous sand. Relations of type (2) make it obvious that the right part constitutes the potential and the rate will be constantly decreasing. By integrating relations of type (2) the following equations occur:

$$C_3S\_Hydr(t) = C_3S_{init} \cdot (1 - \exp(F_0 \cdot k\_C_3S \cdot t)) \quad (3)$$

$$C_2S\_Hydr(t) = C_2S_{init} \cdot (1 - \exp(F_0 \cdot k\_C_2S \cdot t)) \quad (4)$$

$$C_3A\_Hydr(t) = C_3A_{init} \cdot (1 - \exp(F_0 \cdot k\_C_3A \cdot t)) \quad (5)$$

Through the equations (3)-(5) if the specific rates are given, the hydrated parts of the active phases of the clinker can be calculated as function of time, and consequently so can the hydrated fractions. The specific hydration rates are a function of the three phase's particle size distribution. Since the measurement of the particle size for each mineral phase would demand a significant amount of time and equipment, the following cumulative measurements of the cement fineness were taken into consideration:

(a) % Residue in the sieve of 40 microns, R40

(b) Specific surface, Sb in cm^2/gr

Specific rates were correlated with the fineness by applying the equations (6) – (8):

If the statistically significant among the 9 constants k0,k1,k2 connected to the three phases are estimated, based on experimental data, then the specific rates may be calculated.

$$k\_C_3S = k0\_C_3S \cdot R40^{k1\_C3S} \cdot (\frac{Sb}{100})^{k2\_C3S} \quad (6)$$

$$k\_C_2S = k0\_C_2S \cdot R40^{k1\_C2S} \cdot (\frac{Sb}{100})^{k2\_C2S} \quad (7)$$

$$k\_C_3A = k0\_C_3A \cdot R40^{k1\_C3A} \cdot (\frac{Sb}{100})^{k2\_C3A} \quad (8)$$

Each hydrated phase contributes to the cement strength by Y_Hydr(t). Consequently, strength can be regarded as the product of the contributions with a vector of coefficients. This relation is provided by the equations (9) and (10), where the percentage of clinker, %Cl, has also been taken into account.

Standard siliceous aggregates:

$$Str(t) = \frac{\%Cl}{100} \cdot \begin{pmatrix} C_{C_3S} \cdot C_3S\_Hydr(t) + \\ C_{C_2S} \cdot C_2S\_Hydr(t) + \\ C_{C_3A} \cdot C_3A\_Hydr(t) \end{pmatrix} \quad (9)$$

Calcareous sand containing small clay amounts:

$$Str(t) = \frac{1}{1 + k_R (\frac{\%Clay}{\%Clinker})^{nR}} \cdot \frac{\%Clinker}{100} \cdot \begin{pmatrix} C_{C_3S} \cdot C_3S\_Hydr(t) + \\ C_{C_2S} \cdot C_2S\_Hydr(t) + \\ C_{C_3A} \cdot C_3A\_Hydr(t) \end{pmatrix} \quad (10)$$

Where Str(t) the compressive strength of cement specimen within a time interval t since their preparation in Mpa and C_Y the differential strength coefficients for every phase. The natural meaning of each coefficient is that when a phase is 1% hydrated, the cement strength increases by C_Y. If the three parameters C_Y are calculated, based on experimental data, the strength of a specific type of cement can be estimated as a function of time. The coefficient k_R and the exponent nR express the retarding action of the clay concerning the strength development.

4 Calculation of Parameters

4.1 Standard siliceous sand

To estimate the parameters mentioned in paragraph 3, the following technique was applied. As input variables the following were considered:

(a) Mineral composition of clinker.
(b) Percentage of clinker.
(c) Residue R40
(d) Specific surface Sb
(e) Curing time of the specimen.

The compressive strengths of the specimen constituted the output variable. Through the least-square method and non linear regression the optimal coefficients of the influence of fineness on the specific rates k0,k1,k2 and of the differential contribution of each phase to the strength C_Y were calculated , in order to minimize the errors between the calculated strengths and the actual ones. For a set of 202 experimental points, the optimization of these parameters gave a standard error between the actual and the calculated value, s_str = 1.97 Mpa and regression coefficient R=0.993, which are definitely acceptable.

Table 5. Kinetic parameters values.

Parameter	Value
C_{C3S}	0.762
C_{C2S}	1.378
C_{C3A}	1.344
k0_C3S	$1.31 \cdot 10^{-5}$
k1_C3S	-0.134
k2_C3S	2.92
k0_C2S	$1.26 \cdot 10^{-9}$
k1_C2S	-0.229
k2_C2S	4.67
k0_C3A	$5.33 \cdot 10^{-2}$
k1_C3A	0.00
k2_C3A	1.00

The values of the optimum parameters are shown in the Table 5. In Figure 1 the strengths calculated through the mathematic model as well as the actual strengths are displayed. In the Figure 2, the actual and estimated from the model strengths, for samples of different fineness and clinker contents are demonstrated.

The following conclusions occur from Table 5:

- As far as the hydration of C_3A which is significantly faster than this of the two other phases is concerned, the influence of the cement fineness is significantly smaller than it is in the case of C_3S, C_2S.

- The influence of the residue R40 is more important in the case of hydration of C_2S than it is in this of C_3S.

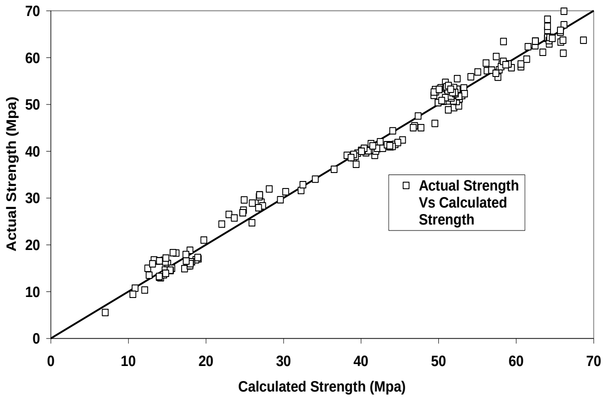

Figure 1.Experimental and model results.

Since the two fineness parameters R40, Sb are not independent of each other, if the model is intended to be utilized for composition designing, a relation connecting them is necessary. For a specific cement mill and for products of several points of the circuit, the following relation has been extracted:

$$\frac{Sb}{100} = -11.23 \cdot \ln(R40) + 57.24 \qquad R = 0.99 \quad (11)$$

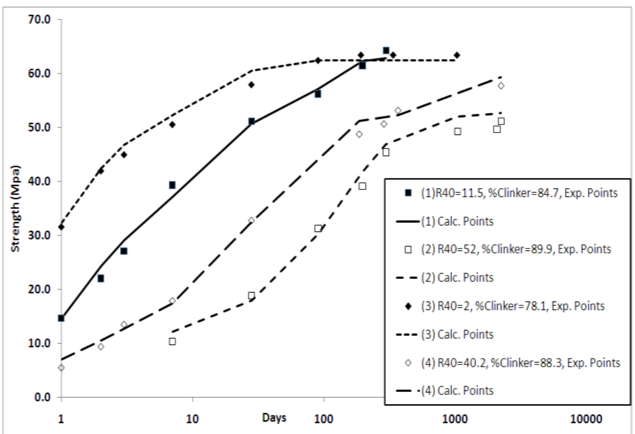

Figure 2.Actual and model results for different %R40 and %Clinker.

The correlation of the specific surface with the residue is undoubtedly a function of the grinding media composition as well as this of the separator. However, the relation above can be safely used as guidance for designing.

4.2 Calcareous sand containing small clay amounts

The model parameters were estimated through non-linear regression techniques as in the previous case by fitting 73 experimental points taken in curing ages from 1 day to more than 1000 days. As exponent values k1_Y, k2_Y of the equations (6), (7), (8), where Y is the clinker mineral phase, were taken the calculated previously appearing in the table 5. These values were found for the same cement types but for a wide range of fineness, so are applicable. The same values of the coefficients k0_Y are calculated, independently of the aggregates type used. As a result, the values of 11 model parameters were estimated, demonstrated in the table 6, where the corresponding standard errors also appear. In Figure 3 the strengths calculated through the mathematic model as well as the actual ones are shown.

Table 6. Model parameters

Siliceous sand		Calcareous sand	
Parameter	Value	Parameter	Value
C_{C3S}	0.52	C_{C3S}	0.31
C_{C2S}	0.51	C_{C2S}	0.90
C_{C3A}	5.95	C_{C3A}	8.02
k0_C3S	$1.04 \cdot 10^{-6}$	F_0	1.52
k0_C2S	$1.12 \cdot 10^{-7}$	k_R	13.9
k0_C3A	$1.42 \cdot 10^{-2}$	n_R	2.53
Std. Error	1.45	Std. Error	2.73

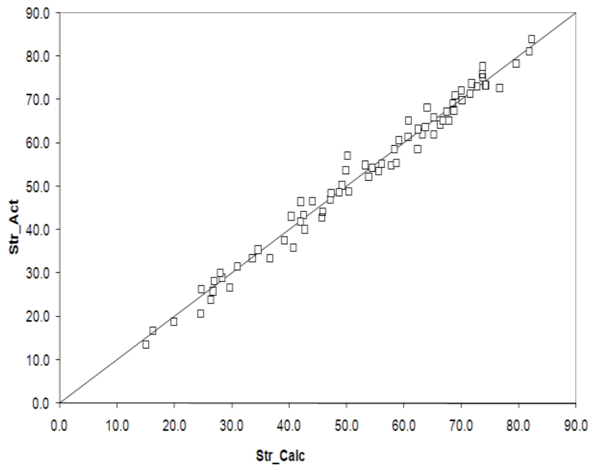

Figure 3.Experimental and model results

The experimental and calculated from the models strengths as function of time for the two cement types examined and all the aggregates are presented in the Figures 4 and 5. From these it is observed that the mortars derived using pure calcareous sand provide strength higher enough than the corresponding mortars produced with siliceous sand. For this reason the parameter F_0 is significantly higher than one. Approximately, the 2 days strength of the calcareous sand test – alternative test - provides results similar to the 7 days of the EN 196-1 standard test. The 7 days of the alternative test seems to be a good approximation of the 28 days. The above means that laboratory tests using calcareous sand instead of the siliceous one could give a prediction of the 28 days strength in an earlier age.

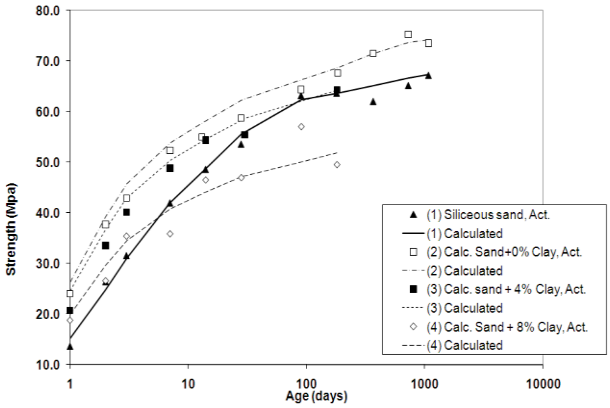

Figure 4.Experimental and model strength results vs. time for CEM II A-L 42.5 R

As the time increases the difference in strength seems to be lower. This fact has to be attributed to the following reasons:

- The different shape of the crushed limestone aggregates in relation with the spherical siliceous sand particles.
- As a result of the previous the specific surface of the calcareous sand is higher than this of the siliceous sand.
- The higher population of active centers in the case of calcareous sand in relation to the siliceous one results in enhanced initial hydration rates.

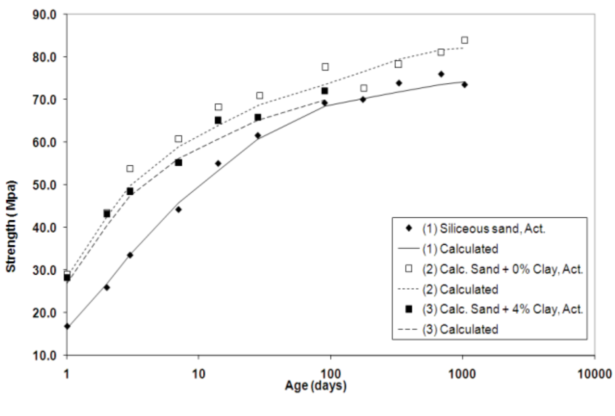

Figure 5.Experimental and model strength results vs. time for CEM I 52.5 N

The inhibiting effect of the clay is obvious from the Figures 4 and 5. This effect is taken into consideration in the model presented by the two parameters k_R, n_R. The high values of these two parameters prove that clay inhibits considerably the achievement of a strength target by applying a convenient cement or mix design and supposing pure aggregates.

5 Application of the Model

5.1 Influence of the cement fineness on the hydration of the mineral phases

To investigate the impact of the cement fineness on the hydration of the clinker mineral phases as function of time a typical cement CEM II A-L 42.5 is considered, with clinker content, %Cl=82.7% and clinker mineral composition: C_3S = 61.9, C_2S = 15.3, C_3A = 7.1. Two cases of fineness are investigated: R40=8% and R40=16%. By utilizing equation (11) the corresponding specific surfaces are calculated. Then the kinetic model is applied for ages from 1 day up to 1000 days for siliceous aggregates. The results are demonstrated in the Figure 6 and the following conclusions can be extracted:

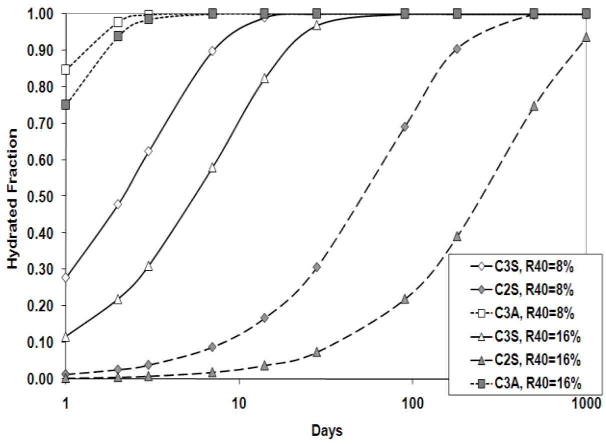

Figure 6.Hydrated fractions of the clinker phases

- The C_3A is fully hydrated in 7 days for the fineness range investigated.
- The C_3S of the cement with R40=8% is completely hydrated in 14 days while the C_3S of the coarser cement is around fully hydrated after 28 days.
- As concerns C_2S, the 90% is hydrated after 180 days in the case of the fine cement, while in the case of the coarse cement the 94% is hydrated after a period of 1000 days.

5.2 Influence of the cement fineness on the compressive strength

The strengths of the cement CEM II A-L 42.5 for ages of 28, 90, 180 days were calculated, based on the parameters given in Table 5 and through the relation (9). The results are displayed in Figure 7. Several experimental values are also displayed in the same figure. The fitting of the model to the experimental values is adequate. It also occurs from this figure that after 28 days the development of strengths continues and practically after the age of 90 days the cement moves on to a higher class of strength. It also occurs that for a given cement composition and clinker quality, by regulating the fineness, any target of strength covering this given class, may be achieved.

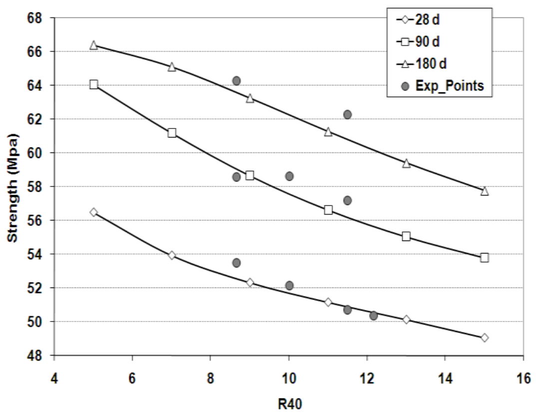

Figure 7. Influence of the to cement fineness on the compressive strength

5.3 Influence of the clinker mineral composition on the compressive strength

The influence of C_3S on cement strength of 7 and 28 days as well as this of the C_3A on the strength of 1 and 2 days were estimated. The calculations were based on the results of the proposed model and on analysis of clinker received from the data of the quality control department in Halyps Laboratory.

The results are displayed in Figure 8. To receive these results, composition data of cement CEM II A-L 42.5 were utilized. The results confirm that the C_3S contained has a significant effect on the strengths of 7 and 28 days, for a value of up to 59%. Beyond this value its influence does not seem important. Furthermore the value of C_3A affects significantly the early strengths of the cement.

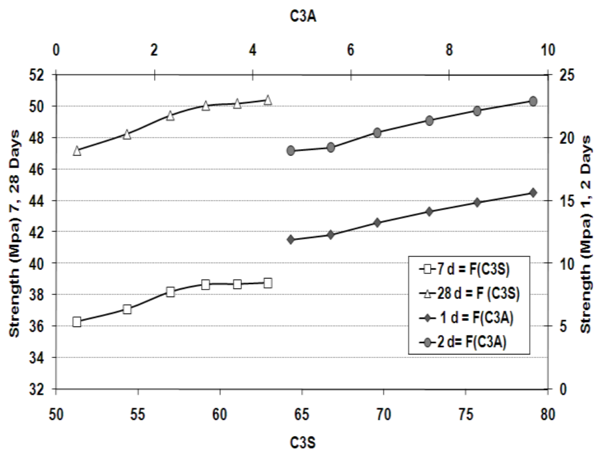

Figure 8. Impact of the clinker mineral composition on the compressive strength

Consequently it is possible with the appropriate regulation of the kiln feed, to produce clinker of the desired properties as to the early and final strengths as well as to their development.

5.4 Analysis of uncertainty in the estimation of strength

The variability of the inserted raw materials and the operation of the installations are the basic sources of the variance in the properties of the product. The model that has been developed can be used as a tool for the estimation of the influence of each deviation to the total deviation of strength. Undoubtedly these results must not be taken absolutely into consideration but rather as a guide to the estimation of the significance of each introduced variability to the final strength uncertainty, which has been calculated through the following relation, provided by the ENV 13005 standard [12]:

$$u_y^2 = \sum_{i=1}^{N} \left(\frac{\partial y}{\partial x_i} \right)^2 \cdot u_i^2 \qquad (12)$$

Where y = strength for various ages and x = several input variables. Standard deviations are considered as measures of uncertainty u_i. The probable covariance between the input parameters has not been taken into account. The partial derivatives in relation (12) are calculated numerically, using central differences. The absolute value of each derivative expresses the differential influence of the strength if the standard deviation is 1, so they constitute the contributions c_xi. For every input variable the coefficients c_xi have been calculated for several curing ages. The results are given in table 7.

Table 7. Uncertainty coefficients for strength

	Age (Days)			
Coefficient (Mpa)	2	7	28	90
| C_R40 |	1.3	1.6	0.6	1.0
| C_%Cl |	0.2	0.4	0.6	0.7
| C_C_3S |	0.0	0.3	0.3	0.1
| C_C_3A |	0.9	0.5	0.0	0.0

From Table 7 it occurs that the influence of the fineness, expressed as residue in 40 microns, is important for every age. As far as the influence of the percentage of clinker is concerned, for uncertainty of 1% in the composition, it can be neglected in 2 days strength; it increases in 7 days and finally varies in the range of 0.6-0.7 Mpa for older ages. The influence of C_3S can be neglected in the age of 2 days, becomes important in 7 and 28 days and finally declines in 90 days. As to the influence of C_3A, it is most significant in the ages of 2 and 7 days. With no doubt the contributions mentioned above are approximate because the factors of covariance have not been taken into consideration.

5.5 Strength differences between the aggregate types

For the two cement types investigated and for each curing age, the mortars difference in strength prepared with pure calcareous and siliceous sand is calculated. The results are shown in the Figure 9.

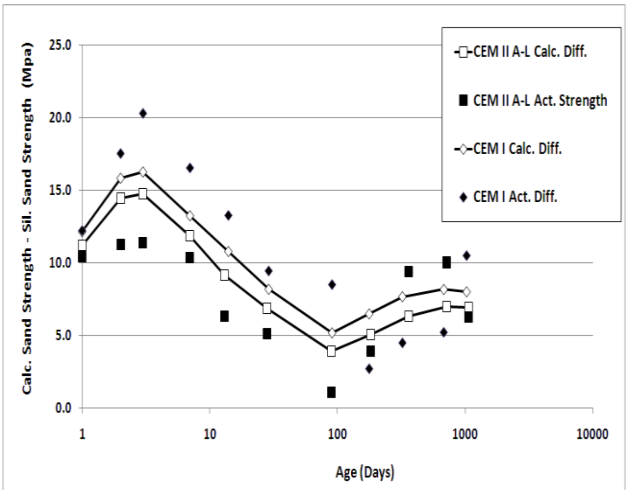

Figure 9. Strength difference between siliceous and calcareous aggregates.

Differences in mortar strength between the two aggregate types for both cements initially pass from an optimum for an age between 2 and 3 days and then drops passing from minimum in around 90 days curing. Then it increases slowly. The above means that the impact of the aggregate type does not vanish in long term but is permanent. So the pure calcareous not only acts as an accelerator of the mortar strength, but provides higher long term strength as well. It is concluded that the shape factor and the larger surface area of the crushed limestone results in a higher strength, because of the bigger number of contacts between the particles. It must also be mentioned that C_2S continues to be hydrated after the 90 days, so the increased number of contacts of calcareous sand, enhances more the compressive strength.

As it can be observed from the Figures 4 and 5 the clay acts not only as in inhibitor of the strength development but also after 6 months the strength is lower enough than this derived from calcareous aggregates. To illustrate better this phenomenon the following difference was considered: Strength Calc. Sand – Strength Calc. Sand with 4% Clay. The results are shown in the Figure 10 in control chart format.

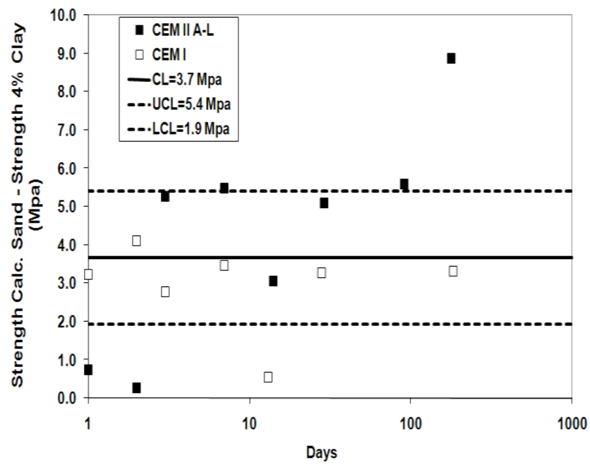

Figure 10. Strength difference between pure calcareous and mixed with 4% clay aggregates.

A permanent difference appears, independent of the curing time. The average difference or central line – CL – is 3.7 Mpa. The upper and lower control limits – UCL and LSL respectively – are calculated using the standard ISO 8258: 1991 [13]. According this calculation the minimum difference is 1.9 Mpa and the maximum one is 5.4 Mpa. As a result the average difference is significantly higher than 0.

To estimate the fraction of the remaining strength, Str_Fraction(t), in the case that the aggregates are contaminated with clay, the following dimensionless form of strength is considered as function of the curing time t.

$$Str\_Fraction(t) = \frac{Str(\%Clay, t)}{Str\_Calc\_Sand(t)} \quad (13)$$

Where Str_Calc_Sand(t) the strength of specimen containing pure calcareous sand in curing time t, Str(%Clay, t) the strength of specimen containing pure calcareous sand contaminated with %clay, in curing time t.

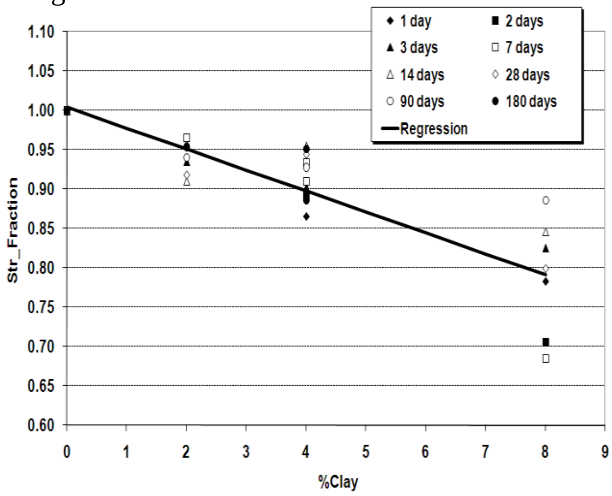

Figure 11. Influence of the clay content to the relative strength

The results are depicted in Figure 11 and fitted to the equation (14) from which is concluded that each 1% clay in the aggregates and for a ratio Aggregates/Cement=3 results in a decrease of the strength by 2.7%.

$$Str\_Fraction(t) = 1.00 - 0.027 \cdot \%Clay \quad (14)$$

According an earlier study [14], a function between concrete strength, cement strength and cement content for a slump S3 was found for a concrete containing cement of strength class 32.5 and 42.5, described by the equations (15) and (16):

$$Str\_Cem = (\alpha \cdot Str\_Cem\_32.5 + (1-\alpha) \cdot Str\_Cem\_42.5) \cdot \frac{Tot\_Cem}{300} \quad (15)$$

Where Str_Cem_32.5, the strength of the cement 32.5, Str_Cem_42.5, the strength of the cement 42.5, a, the mass fraction of the CEM 32.5 in the total cement mass, Tot_Cem

$$Str\_Concr = 2.20 + 0.672 \cdot Str\_Cem \quad (16)$$

A C25/30 concrete with a strength 38 Mpa can be produced with an amount of 315 Kg/m^3 of CEM 42.5 with an average strength 52 Mpa. In case that the aggregates have contained 2% clay, then the concrete strength becomes 36.1 Mpa. Probably the strength drop is more, due to the fact that in the actual concrete the Aggregates/Cement > 3. In this case to compensate the clay impact the concrete producer has to increase the cement quantity by 15 Kg/m^3 which is apparently a highly costly but required action as concerns the product quality.

5.6 Impact of the aggregates nature to the mortar strength standard deviation

To study the influence of the nature of aggregates - silica sand, calcareous sand or mix calcareous sand with clay – the standard deviation of the 6 individual strength results becoming from the prisms according to the norm EN 196-1:2005 was investigated. This is the “within test” standard deviation. Higher the standard deviation less constant the mortar and correspondingly the concrete produced.

The standard deviation as function of the aggregates nature is plotted in Figure 12 in control chart form according to the ISO 2858:1991 [13]. As it can be seen starting from an average standard deviation of 0.9 Mpa using standard silica sand, the preparation of specimen with calcareous sand augments the deviation in the region of 2 Mpa. The addition of clay increases further the standard deviation and for clay content equal to 8%, the deviation becomes very high because the mortar is of low workability. This is due to the water absorption from the clay.

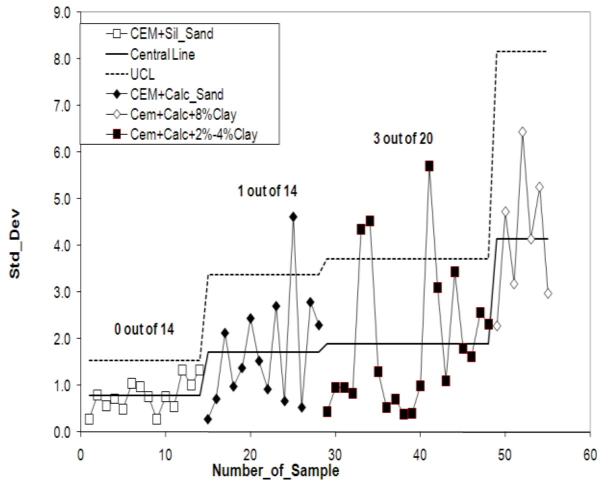

Figure 12. Strength standard deviation as function of the aggregates type

6 Conclusions

In the present study a kinetic model of cement strength development was created, based on the hydration of its active phases. For this purpose measurements of cement fineness, composition of clinker and compressive strengths were utilized. The model was applied in mortars composed from different cement and aggregate types. Two cement types were used – CEM I and CEM II A-L – and two basic aggregates – siliceous and pure calcareous sand of the same particle size. To investigate the impact of the clay on the compressive strength development, the fines of the calcareous sand were replaced with different portions of clay.

For the cements CEM I and CEM II A-L and siliceous sand this model predicts with a standard error of around 2.0 Mpa for ages starting from 1 day up to 5.5 years, for a wide range of input variability. This model may be utilized for the production design of specific types of cement, with their properties fully determined. If the values of the properties mentioned are taken for granted there is a possibility for:

- Designing of a realizable composition of clinker that has a specific mineral analysis. Once this composition is determined, the raw materials that will realize it may be selected.
- Designing of cement composition.
- Determination of the fineness target and choice of the production operation parameters.

The model can also be utilized as a tool for the current quality control and the quality assurance of the production. In case for instance, that the model predicts deviation from the target, it provides traceability so that the cause of this deviation may be found and corrected. Furthermore, if there is a deviation in some input variable there is the option of intervention on some other variable, in order for the influence of the first one to be eliminated.

In the case of the calcareous aggregates, pure or partially mixed with clay, the model presents a standard error of 2.7 Mpa for curing ages up to 1000 days, significantly higher than the previous case, but adequate for the strength range measured. The pure calcareous aggregates provide a significantly higher compressive strength than the siliceous ones, due to their non spherical shape providing an elevated specific surface area and causing a larger number of contacts between the particles. The differences in strength pass from a maximum value of ~15 Mpa after a curing of 2-3 days, then from a minimum difference of ~ 5 Mpa in 90 days curing. In long term - ~1000 days curing – a permanent difference of 7-8 Mpa remains. The fine clay added in the limestone aggregates, not only inhibits the strength development, but also gives rise to a considerable drop of the mortar strength.

Aggregates nature has a strong impact on the strength variance. The strength of mortars containing calcareous aggregates presents the double standard deviation compared with the corresponding prepared with siliceous sand, caused by the lower workability of the mortar. The existence of clay deteriorates further the strength variance.

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