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*Penza State University of Architecture and Construction*

*Ph. D. in Engineering,*

*Assoc. Prof. of Department of Technology of Concretes, Ceramics and Binding Agents*

*A. V. Lakhno*

*Engineer of Department of Technology of Concretes, Ceramics and Binding Agents*

*O. A. Kuvshinova*

*Russia, Penza, tel.: +7(8412)49-72-77; e-mail: office@pgasa.ru*

*Moscow State University of Railways*

*Ph. D. in Engineering,*

*Assoc. Prof. of Department of Building materials and Technologies*

*P. V. Voronov*

*Russia, Moscow*

A. V. Lakhno, O. A. Kuvshinova, P. V. Voronov

## **ASSESSMENT OF KINETIC PROCESSES OF HARDENING OF BUILDING MATERIALS**

**Problem statement.** Kinetic processes are of huge importance when producing building units and operating them as well. However, both technological and operation parameters are determined by the structure of a material under study.

**Results and conclusions.** Kinetics with asymptotic approximation at hardening of building materials is analyzed. The validity of use of new kinetic equation is proved, characterizing harden composite systems and taking into consideration structural and topological peculiarities of new solid-like phase formation directly effecting the evolution of the processes. Results of research of change of strength at solidification a cement-sandy solution with various additives are submitted.

**Keywords:** hardening, kinetics, composite, fractals, phases, additives.

### **Introduction**

Kinetic processes are of huge importance when producing building units and operating them as well. In operating practices they manifest themselves as creep, relaxation, shrinkage,

bulking, corrosion, etc. However, both technological and operation parameters are determined by the structure of a material under study. Technological materials are, as a rule, heterogeneous systems including several stages separated by a sharp phase boundary [1, 2].

### **Model analysis of kinetics with asymptotic approximation by a perturbation method**

Let us perform a model analysis of kinetics with asymptotic approximation, as the process of change of the material strength at solidification. For this purpose, let us use a perturbation method which implies that if a stabilized parameter  $x_m$  is changed by a quantity  $\Delta x = x - x_m$  at the expense of the external perturbing action which is subsequently turned off, as time passes, the parameter  $x$  spontaneously regains its asymptotic limit corresponding to a kinetically stabilized value  $x_m$ . According to this model, the dynamic equation will look like:

$$dx/dt = -k(x - x_m) \quad (1)$$

With the aim of simplifying calculations, a new variable  $z = x - x_m$  is introduced.

At the initial moment of time the condition  $t_0 = 0$ ,  $x_0 = 0$ ,  $z_0 = -x_m$  is satisfied. The value  $x_m$  is constant, since it correlates with the limit of kinetic asymptotics  $x = f(t)$ .

According to this, we get  $dz = dx$ . The simplifications performed allow to write the function (1) in the classical form:  $dz/dt = -kz$ . As a result of separation of variables, we have  $d \ln z = -k dt$ .

Integrating the deduced equation within the limits of  $t_0 \dots t$  and  $z_0 \dots z$ , we find that

$$x = x_m (1 - e^{-kt}) \quad (2)$$

The equation obtained is a universal form of kinetic laws with asymptotic approximation of a parameter under study and is valid for homogeneous systems where the influence of separate structural elements is either suppressed by global processes or it is insignificant. The application of the function (1) only does not allow to conduct the equally successful description of significantly different kinetic lines. For these curves the equation (2) yields merely an approximate description. The calculated values quite frequently have a prohibitively large divergence from the experimental data.

In order to obtain more sufficient calculation results, we use complex empirical relation like

$$x = x_m (1 - e^{-kt^n}), \quad (3)$$

where  $n$  is a constant empirical coefficient.

The discrepancy between the basic equation (2) and the empirical one (3) which testifies the initial kinetic model leading to the empirical equation (3) is incomplete, as applied to heterogeneous systems.

In the original equation (1) the prominent fact that the speed of the parameter  $x$  change is proportional not only to the value of the parameter proper but also to the characteristic structural size of the composite material is not taken into account. In essence, the assumption made was basic to the working out a new model.

According to the expounded hypothesis, the original dynamic equation (1) takes the following form:

$$dx/dt = -kxl_i, \quad (4)$$

where  $l_i$  is a characteristic structural relative size of a composite system which is a geometric index expressed through the system dimensionality and depending on the argument parameter.

At  $l_i = 1$  the relation (4) takes the classical form (1), which is in conformity with the succession principle. Thus, either the index of linear surface or solid structures or similar indexes of fractal formations may be manifested by the size  $l_i$  [3].

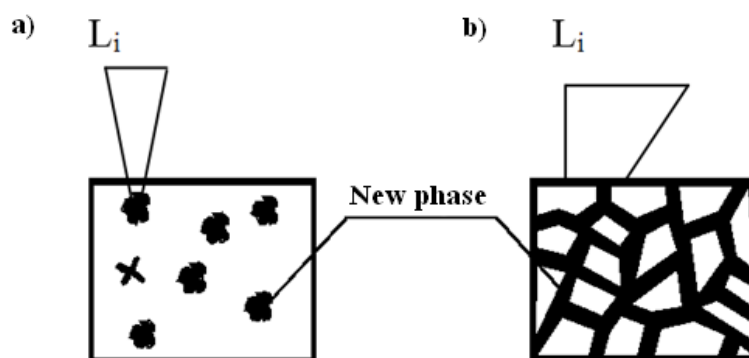
Since composite heterogeneous systems have several phases, the relation (4) does not lead to the obvious conclusion as to which size is to be considered. In order to clear this up, let us write the kinetic relation with asymptotic approximation (1) considering the condition (4) in the following form:

$$dx/dt = k(x_m - x)l_i. \quad (5)$$

In relation to the parameter being examined the sense of the equation is not lost, for the speed of change declines as  $x$  increases. The presented form of the equation allows to characterize

the structural size  $l_i$ . With reference to (5), it can be seen that in the given equation it is the structural size the increase of which leads to an increase in the speed of the observed parameter  $x$  change that should be primarily considered.

Besides, the stage continuous length has a direct influence on how the kinetic processes follow. Its index is a linear size (average size of isolated clusters, average size of a perlocation carcass cell, etc.). Lots of characteristics are quite sensitive to the topological state of a phase. Thus, the strength controlled in the process of a composite hardening is sensitive to the topological state of a volume part that turned into a solid phase. When a new solid phase is distributed in the volume in the form of isolated inclusions (fig. 1a), it is not capable of exerting any influence on the strength. If a solid phase has a continuous topological coherence throughout the whole volume (fig. 1b) spatial structural stiff carcass is formed, which leads to an increase in a composite material strength. Here, the system structural size is an average relative linear size  $l_i$  of a structural spatial reinforcing carcass.



**Fig. 1.** Models of a new phase distribution in a composite system volume

The crystallite phase growth occurs as a result of the attachment of kinetic particles of matrix environment due to their random motion. The Fig. 2 schematically depicts the trajectories of the particles in the matrix volume  $V_i$ . The ambient crystallite mass where the trajectory ends is taken as the volume  $V_i$  limit. Returns and self-intersections are common for a random walk trajectory as contrasted to the solid phase carcass curve.

In dynamic processes, the average value of a vector's magnitude linking the beginning and the end of the random walks trajectories (see Fig. 2) for the time  $t$  is determined by the relation (2):

$$r = \sum_i^N r_i / N \propto t^H, \quad (6)$$

where  $H$  is the Hurst index,  $1 \geq H \geq 0$  which holds for tasks both on a plane and in space.

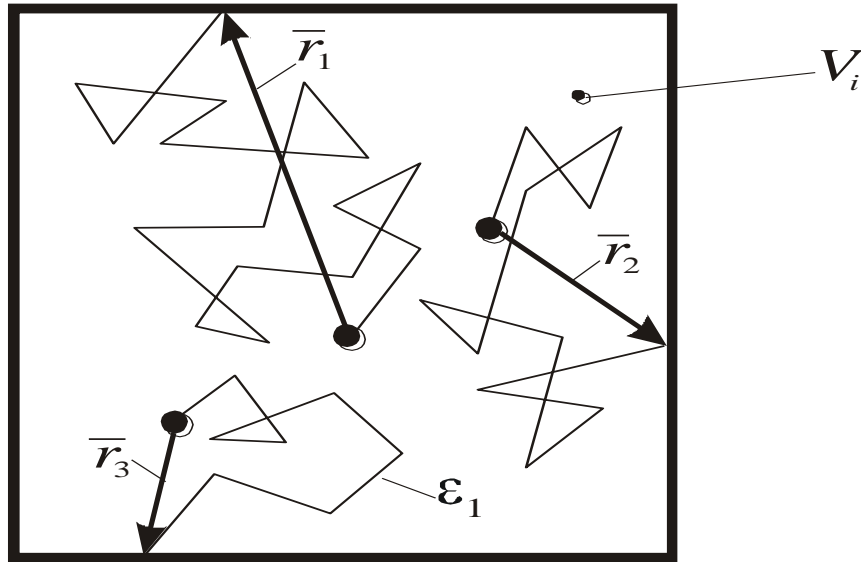


Fig. 2. Model of kinetic particles random walks

At the invariant average speed of active particles movement the random walk time  $t$  is proportional to the volume  $V_i$ , whence we have the following:

$$l_i \propto V_i^H, \quad (7)$$

where  $l_i \approx 2r$ . The values  $l_i$  and  $V_i$  in the natural dimension are connected by the relation

$$l_i^{D_i} = V_i, \quad (8)$$

where  $D_i$  is a system internal dimensionality. For a fractal general case for a we can write  $l_i^{D_i} \propto F_i$ .

According to (7) and (8) the internal fractal curve dimensionality in space is

$$D_i = 1/H \quad (9)$$

and determined in the interval  $\infty > D_i > 1$  which goes beyond the concept of physical space.

However it is located in the accepted interval of dimensionality values.

Comparative analysis of the equations  $D_e = 3-2H$  and (9) shows that the external  $D_e$  and internal  $D_i$  dimensionalities coincide with the topological dimensionality  $d$  for non-fractal lines

$$D_e = D_i = d = 1 \quad (H = 1)$$

and smooth surface objects

$$D_e = D_i = d = 2 \quad (H = 0.5).$$

In its turn, they are different

$$D_e = d = 3 \quad (H = 0)$$

for bulk smooth areas, whereas

$$D_i = \infty \quad (H = 0).$$

Since the Hurst index for the dimensionalities  $D_e$  and  $D_i$  is invariable, we get the following:

$$D_e = 3 - 2/D_i \quad \text{or} \quad D_i = 2/3 - D_e \quad . \quad (10)$$

Let us examine the dynamics of phase transition on the model of the external curve  $L_e$  filling of a meaningful volume  $V_m$ . The pace of the curve volume filling is determined by the expression:

$$dV/dL_e = q(V_m - V), \quad (11)$$

where  $V$  is the volume with a complete phase transition (filled with the curve  $L_e$ ),  $q$  is a constant coefficient. In its turn,  $\varepsilon$ -resolving power hyperbolically decreases through time, since the filling curve becomes more and more winding on small scales.

$$\varepsilon = bt^{-1}, \quad (12)$$

where  $b$  is a constant value. Substituting  $L_e = a\varepsilon^{H-1}$  and (12) into (13) gives a dynamic relation

$$dV/d(t^{1-H}) = k(V_m - V), \quad (13)$$

where  $k = qab^{H-1}$ . The solution (13) leads to a kinetic equation for a phase transition with an external asymptotic limit  $V_m$ :

$$V = V_m [1 - \exp(-kt^{1-H})]. \quad (14)$$

The comparison of (3) with (14) shows that  $n = 1 - H$ .

Hence a certain type of a kinetic function as such is conditioned by a topological state and phase variability in heterogeneous systems. In the original prerequisites of the model presented the initial condition of the formation of a percolating mass of a new (external) phase is presupposed. Thus, generally the equation (14) evaluates the kinetic processes out of solid phase percolation ( $3 \geq D_e \geq 1, +\infty \geq D_i \geq 1$ ).

Experimental research of strength change in the process of cement-sand grout solidification were conducted with the following additives: refined native levorin solution (RNLS), Sica Viscocrete and Sica Viscocrete: and +RNLS. The results of the experiment are presented in the Fig. 3.

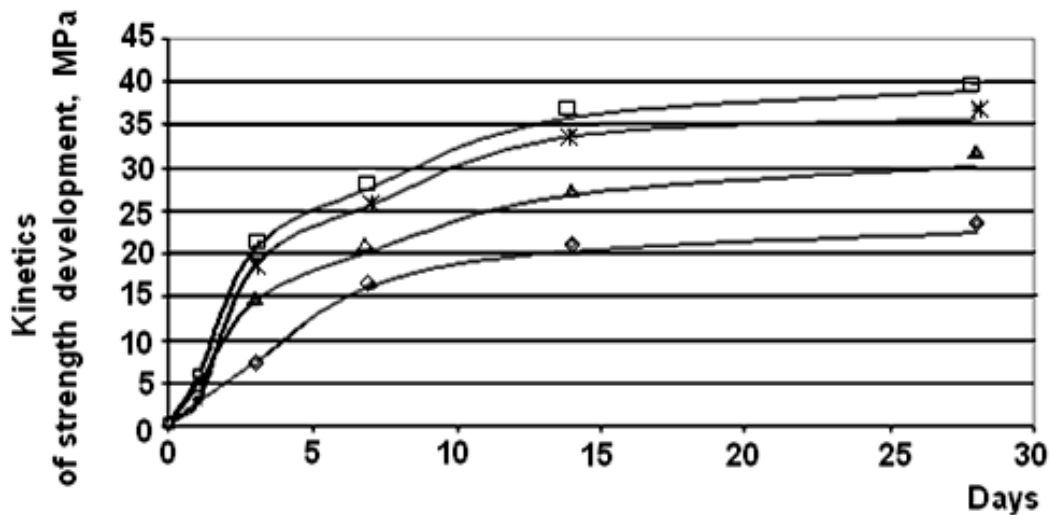


Fig. 3. Kinetics of Sary Oskol cement M500 strength sets:

◇ — control composition; △ — with the additive RNLS; ✱ — with the additive Sica Viscocrete;  
□ — Sica Viscocrete +RNLS

The experimental examination in the relations (3) and  $n = 1 - H$  showed the following: control composition value is  $n = 0.472$ ,

–  $n = 0.423$  for the composition with the additive RNLS,

- $n = 0.31$  for the composition with the additive Sica Viscocrete,
- $n = 0.439$  for the composition with the additive Sica Viscocrete +RNLS.

According to the relation,  $1-H = (D_e-1)/2$ :

- $D_e = 1.944$  for the control composition,
- $D_e = 1.846$  for the composition with the additive RNLS,
- $D_e = 1.62$  for the composition with the additive Sica Viscocrete,
- $D_e = 1.868$  for the composition with the additive Sica Viscocrete +RNLS.

According to the calculations made, solid-phase new formations predominantly have a platelet shape.

### Conclusions

Hence the initial condition of the formation of a percolating mass of a new (external) phase is presupposed. Thus the equation  $V = V_m [1 - \exp(-kt^{1-H})]$  evaluates the kinetic processes out of a solid-phase percolation:  $3 \geq D_e \geq 1$ ,  $+\infty \geq D_i \geq 1$ .

The latter above all are kinetic processes of the material physical-mechanical properties change at phase transitions «liquid  $\rightarrow$  solid body».

By and large the generalized equation (14) features not only the kinetics of phase transitions in solidifying composite systems but it also reflects the topological features of a phase state having a direct influence upon the evolution of the processes.

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