Aspects of the kinetics of the formation of capillary-porous structures of foam concrete as low-carbon technology

Svetlana Samchenko1 and Vladimir Kulikov1*

1 Moscow State University of Civil Engineering, 129337 Moscow, Russia

Abstract. At the present stage, materials used within the framework of low-carbon technology are becoming increasingly in demand. The purpose of the study was to identify and study the analytical dependencies of technological parameters and aspects of the preparation of foam concrete depending on the concentration of foaming agents (surfactants) at various points in the formation of the capillary-porous structure of foam concrete as low-carbon technology. The law of acting masses was adopted as the main basis for assessing the kinetics of interaction of light concrete components with surfactants. This thesis is interpreted taking into account the fact that the ratios between the concentrations of reagents and their products at a discrete time are considered to be constant. The questions of estimating the speed of the processes are formalized. In contrast to the traditional approach, the material is considered from the standpoint of implementing calculations using analytical algorithms for solving direct and inverse kinetic problems. The issues of effective use are considered. The literature on technical kinetics practically does not address the issues of specific practical implementation of kinetic calculations. Dynamic models for estimating and controlling the kinetics of the formation of pore structures have been developed. The practical use of the developed dynamic models makes it possible to evaluate and promptly adjust the parameters of foam concrete of the formation of capillary-porous structures of foam concrete as low-carbon technology

1 Introduction

Some aspects of the kinetics of the formation of capillary-porous structures as early as 1934 were described in the analysis of new types of light concrete in the works "Theory of concrete strength" [1], "New types of concrete" [2], B.G. Skramtæv. Lightweight concretes were classified into: - fine-pored and coarse-pored and, concretes with porous aggregates.

Cellular concrete and concrete with jellies (C-concrete) were assigned to the first group, concrete without fine aggregate was assigned to the second group, and quick-hardening lime-treplel cinder concrete with quicklime and brick concrete were assigned to the third group.

* Corresponding author: 9646379164t@mail.ru

© The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (https://creativecommons.org/licenses/by/4.0/).
In these works, B.G. Skramtaev for the first time pointed out that for the types of light concrete that were new at that time, the assessment of their strength only by the water-cement factor was insufficient.

We agree, taking into account the further use of ideas that the interaction of clinker minerals of binders with water, even without surfactants, is a complex phenomenon [3], as a result of which hydrosilicates, hydroaluminates, calcium hydroaluminites of various chemical and mineralogical composition are formed.

That is:

\begin{align}
2(3\text{CaO SiO}_2) + 6\text{H}_2\text{O} &= 3\text{CaO SiO}_2 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2 \\
2 \text{CaO SiO}_2 + 3\text{H}_2\text{O} &= \text{CaO SiO}_2 2\text{H}_2\text{O} + \text{Ca(OH)}_2 \\
3\text{CaO Al}_2\text{O}_3 + 6\text{H}_2\text{O} &= 3\text{CaO Al}_2\text{O}_3 6\text{H}_2\text{O}
\end{align}

(1-3)

It is known [4] that the formed calcium hydroaluminate in the initial setting period, due to its instability, leads to a certain decrease in the strength of the cement stone. But since in the aqueous cement system, due to the addition of two-water gypsum introduced during clinker grinding, there are always ions (SO_4)^2- calcium hydroaluminate binds at the beginning of the hydration process to the highly sulphate form of calcium hydrosulfoaluminate, ettringite:

\begin{align}
3\text{CaO Al}_2\text{O}_3 + 3\text{CaSO}_4 + (31-32)\text{H}_2\text{O} &= 3\text{CaO Al}_2\text{O}_3 3\text{CaSO}_4 (31-32)\text{H}_2\text{O}
\end{align}

(4)

If (SO_4)^2-ions are not enough [5] for the complete binding of calcium hydroaluminates to ettringite, then low-sulfate forms of calcium hydrosulfoaluminate can be formed:

\begin{align}
2(3\text{CaO Al}_2\text{O}_3 .6\text{H}_2\text{O}) + 3\text{CaO Al}_2\text{O}_3 3\text{CaSO}_4 (31-32)\text{H}_2\text{O} + 10\text{H}_2\text{O} &= \\
= 3(3\text{CaO.Al}_2\text{O}_3. \text{CaSO}_4 18\text{H}_2\text{O})
\end{align}

(5)

Then, if the left parts of equations (1-5) are represented by the scheme of interaction of the initial components without surfactants, as (A+B), then all the right parts of the above expressions of kinetic processes without surfactants (1-5) can be represented by the scheme: (C+D) and, or in general: - (A+B) = (E).

2 Relevance of the work

A new generalizing theory of strength of concrete of different types can be based on the following, the third theory of strength, destruction, taking into account the rate of formation of capillary-porous structures [6,7].

Some uncertainty in this interpretation [8] is due, among other things, to the fact that modern mineral binders, by definition, are powdery materials that, after mixing with water, and in some cases with aqueous solutions of salts, acids, surfactants (surfactants), form a plastic workable mass, gradually solidifying and turning into a solid state. Such a definition only fixes the fact of solidification of the substance and does not disclose the constituent parameters of this complex and diverse kinetic process.

Thus: - these are compositions based on heterogeneous dispersed systems of the "solid – liquid" type, the components of which enter into physicochemical interactions in various phase states, forming a plastic mass that eventually turns into artificial stone.

At the same time, researchers pay little attention to mathematical models of the formalization of the kinetics of the formation of artificial stone with specified capillary-porous characteristics.
3 Research methodology

To formalize [9, 10] the processes of the considered systems, we will highlight the path that they take in the process of converting the initial components into products of interaction with surfactants.

The rate of interaction is defined as the change in the amount of reacting substance per unit of time assigned to the unit of reaction space. Depending on whether the interaction is homogeneous or heterogeneous, the concept of reaction space is defined in different ways. We will assume that in a homogeneous system the interaction is carried out in the entire volume of the system, in a heterogeneous system - at the interface of phases. Formally, we denote this as follows:

\[ r = \pm \frac{dn}{V \cdot dt} \]  

where: - \( r \) is the reaction rate; \( dn \) is an infinitely small number of reagents; \( V \) is the volume of the reaction space; \( S \) is the area of the contact zone; \( dt \) is an infinitely small period of time.

The sign of the derivative (−) – will indicate that the substance is consumed during the reaction, and (+) - accumulates. If the volume of the system remains constant during homogeneous interaction, then \( \pm \frac{dn}{V \cdot dt} = dC \). The rate associated with the change in the concentration of the reactant over time is defined as:

\[ r = \pm \frac{dc}{dt} \]  

The basic position for solving the direct problem of kinetics is to define the kinetic scheme of interaction reflecting the proposed mechanism of transformation \((A + B) = (E)\). Under the mechanism we will understand a set of elementary stages (elementary interactions), through which the transformation of the initial components into the final products of interaction is carried out.

Taking into account the stoichiometry of the interaction of the components of light concrete with each other (1-5): binder "BB", fine aggregate "H), water "O", surfactant "P" and mineral additives "D", we present this process as follows:

\[ a \cdot BB + b \cdot Z + c \cdot O + d \cdot P + e \cdot D \rightarrow f \cdot p_1 + g \cdot p_2 + i \cdot p_3 + l \cdot p_4 + k \cdot p_5 \rightarrow \]

\[ \rightarrow M \cdot P \]  

where are: - \( a,b,c,d,e,f,g,i,l,k,M \) stoichiometric coefficients for the corresponding components, \( pi \) are interaction products

And since the change in the concentrations of the components over time is different, then:

\[ r = \pm \gamma_i^{-1} \frac{dC_i}{dt} \]  

\[ r = -\frac{1}{a} \cdot \frac{dC_{BB}(t)}{dt} = -\frac{1}{b} \cdot \frac{dC_1(t)}{dt} = -\frac{1}{c} \cdot \frac{dC_2(t)}{dt} = -\frac{1}{d} \cdot \frac{dC_3(t)}{dt} = -\frac{1}{e} \cdot \frac{dC_4(t)}{dt} \]

\[ = +\frac{1}{f} \cdot \frac{dC_{p1}(t)}{dt} = +\frac{1}{g} \cdot \frac{dC_{p2}(t)}{dt} = +\frac{1}{i} \cdot \frac{dC_{p3}(t)}{dt} \]

\[ = +\frac{1}{l} \cdot \frac{dC_{p4}(t)}{dt} = +\frac{1}{k} \cdot \frac{dC_{p5}(t)}{dt} = \pm \frac{1}{M} \]

\[ \frac{dC_{p}(t)}{dt} \]  

We generalize the presented calculations in the kinetic interpretation of the proportionality of the interaction rate to the concentrations of reacting substances as follows:
\[ r = k \cdot P_i \cdot C_i \] \quad (10)

where: - \( k \) is the constant of the rate of interaction, equal to the value of the rate at single concentrations of reacting substances. Suppose that the velocity constant does not depend on the concentrations of substances and time, but depends on temperature.

The exponent at the concentration of «\( n \)» is the order of the reaction for the i-th substance. If the transformation of the initial reagents into products is not accompanied by the formation of intermediates or particles, i.e. proceeds in one stage, then such a reaction will be considered simple, (elementary):

\[ \text{If } A + 2 \cdot B \rightarrow \text{Products, then } r = k \cdot C_A(t)^1 C_B(t)^2 \] \quad (11)

that is, the "orders" of the reaction for each substance are equal to their stoichiometric coefficients.

In (6) we assume that the reaction has the first order for substance "A" and the second order for substance "B". The sum of the orders for each substance determines the general, third order of the reaction (6).

The process of preparing light concretes (3) from the indicated point of view relates to complex reactions [11,12].

The study of the interaction of a light concrete mixture with surfactants will be carried out according to the scheme:

\[ \{(A+B) = (C)\} = \{(D+E) = (F)\} = \{(K)\} \] \quad (12)

where A is a light concrete mixture, B is a foaming agent (surfactant), C is a heterogeneous dispersed medium of a foam concrete mixture, (D+E) are products of hydration of binders in a surfactant medium, F is a homogenizing medium of calcium hydrosilicates with surfactants, K is foam concrete.

This will allow purposefully controlling the chemical-mineralogical transformation and the time evolution of the transition of the reaction system from the initial state \{(starting substances (A+B))\} to the final state (interaction products (K)).

4 Research results

Studies have been carried out and the dependences between discrete concentrations and the resistance of a number of foaming agents over time have been established, Fig.1:

![Fig.1. Dependence of the achieved multiplicity of foaming agents on the current concentration of the foaming agent surfactant](image)

Analytical dependences of the functions of one variable foam multiplicity \( y \) on the concentration of the foaming agent solution \( x \) in the form of \( y=f(x) \) have been established.
for all the studied surfactants. Dependence \( y = f(x) \) for the foaming agent PO-1 is shown in Fig.2:

![Graph-analytical dependence of the multiplicity of the obtained foam, as a function, on the concentration of the foaming agent "Azolate A" in the form: \( y = f(x) = -0.0342x^5 + 0.7083x^4 - 5.3292x^3 + 16.942x^2 - 16.387x + 11.9 \) with accuracy with respect to the resulting regression equation \( R=1 \).](image)

From the analysis of Fig.2, it is obvious that the dependence is linear in small discrete areas.

Having presented a multicomponent and multifactorial process of interaction of the initial components of light concrete (1-5) with surfactants, taking into account the studies conducted and the presented differential dependencies, we obtain a solution: - showing how the order of the reaction under consideration \( (n) \) affects the reaction rate constant \( (k) \) taking into account the current \( (CA) \) and initial \( (CA0) \) concentrations of the surfactant component in generalized coordinates "X and Y" in time "t". The algorithm and the results of the solution are shown in Fig.3:

\[
k = \frac{1}{(n - 1) \cdot t} \left[ \frac{1}{(CA)^{n-1}} \cdot \frac{1}{(CA0)^{n-1}} \right]
\]

\[
\frac{d}{dx} [CA(t)] = -k [CA(t)]^n \quad CA(0) = CA_0
\]

\[
\int_{CA_0}^{CA} \frac{1}{x^n} dx = -k \int_0^t 1 dy
\]

\[
\int_{CA_0}^{CA} \frac{1}{x^n} dx = -k \int_0^t 1 dy
\]

Fig. 3. Algorithm for determining the dependence of the reaction rate constant "k" on the current "CA" and the final value of the concentrations "CA0" of the initial surfactants, as well as on the reaction order

When solving differential dependencies, another parameter influencing the reaction rate constant \( (k) \) is revealed. At different values of the reaction order \( (n) \), the reaction rate constant \( (k) \) changes as follows, Fig.4:

![Algorithm for determining the dependence of the reaction rate constant "k" on the current "CA" and the final value of the concentrations "CA0" of the initial surfactants, as well as on the reaction order](image)
Fig. 4. Algorithm for determining and solving the problem of changing the reaction rate constant \( (k) \) depending on the reaction order \( (n) \).

Obviously, depending on the reaction order, the concentration of the surfactant reagent decreases in various ways with time. We will use this circumstance as a control technological parameter \( (\text{UP1}) \) in the form of a coefficient of the reaction rate constant:

\[
\text{UP1} = \frac{1}{(n-1)t \cdot c_{A}^{n-1} - c_{A0}^{n-1}}
\]

where \( n \) is the reaction order; \( t \) is the interaction time; \( c_{A}^{n-1} \) - current surfactant concentration; \( c_{A0}^{n-1} \) - the initial concentration of surfactants.

Let’s consider the joint use of parameters (14 and 15) in Fig.5 as a computational experiment:

Fig. 5. Algorithm and solution of the problem of determining the current concentrations of components under initial conditions: the initial concentration of components \( A0 = 0.08 \) (curve 1) and \( B0=0.06 \) (curve 2)
Figure 5 confirms the assumption about the linear nature of changes in the kinetics of concentrations at small discrete test sites.

The practical and technological complexity in the processes under consideration is the issue of establishing the initial parameters in the form of either the values of "t0" of the real discrete time of the beginning of interaction (1-5) with surfactants, relative to which all managerial technological operations must be carried out in the future, or the initial parameters of the concentrations of the components involved in the process, or other technological parameters.

We propose to solve this problem by the method of dynamic modeling of the process under consideration {(1-5) + surfactants}, by creating a trigger control system for the real technological process of preparing light concrete, Fig.6:

![Diagram of control system](Figure 6)

**Fig. 6.** Scheme of control of the beginning of the process of interaction of components (1-5) with surfactants for the preparation of light concrete.

The dynamic model presented in Fig.6 consists of a set of graphical blocks representing the components of the object under study (1-5) and functional elements, signal sources in the form of initial values of the processed data of reagents of prepared light concrete with surfactants, virtual recording devices, animation tools, and technological connections directed between them, signal propagation lines. Blocks of various purposes are grouped into block libraries. Each block has a set of configurable parameters.

Hydration of portland cement clinker grains (1-5) it has a steady exponential character, and is displayed by a smooth curve shown in Fig.7 (screenshot of the oscilloscope) of the control circuit:
The process of the beginning of the interaction of the concrete mixture with surfactant is clearly observed in the lower zone of the oscilloscope screen shot, in the form of two corresponding bends of the smooth curve of the hydration process with surfactant, Fig. 8:

![Fig. 7. Exponential curve of the process of hydration of grains of portland cement clinker without surfactants](image)

The critical points of the beginning of the exponential process of forming the capillary-porous structure of foam concrete indicated by the arrows in Fig. 8 allow the technologist to accurately determine the discrete time of the beginning of various processes of interaction between the initial components of the foam concrete mixture in complex dispersed heterogeneous processes and, including at the interfaces of the phases of the components (Gibbs energy). Following the technological regulations for the preparation of foam concrete, having found out the starting point of the already occurring interaction processes, if necessary, make technological adjustments in a timely manner.

![Fig. 8. Control and graphical representation of the beginning of the process of interaction of the concrete mixture with surfactants](image)
5 Discussion

The presented kinetics methodology, along with thermodynamics, represent complex sections of knowledge. The thermodynamic approach to the description of systems is based on considering exclusively the initial and final state of the system and abstracting from the methods of transition of the system from the initial state to the final one. Thermodynamic methods also determine whether a given state of the system is in equilibrium. But thermodynamics does not predict the dynamics of transitions, and does not determine after what time the state of equilibrium will come. This is the difference between thermodynamic and kinetic methods of describing systems.

The sequence of drawing up a calculated dynamic control scheme for the technological process of preparing lightweight foam concrete and removing the results of calculations and modeling is shown in Fig.6-8.

The proposed method of visual-dynamic modeling allows designers of foam concrete to enter a description of the simulated system in a natural for technologists, mainly graphical form, and present the simulation results again in graphical form, for example, in the form of time or phase diagrams. During the simulation, it is possible to observe the processes occurring in the system. For this purpose, special "viewing windows", oscilloscopes and other devices are used.

6 Conclusion

1. Analytical dependences of the stability and multiplicity of foaming agents on the current concentrations of the initial components are obtained.
2. The integral dependence of the interaction rate constant "k" on the initial and current concentrations of the reagents of the foam concrete mixture is substantiated and obtained.
3. The analytical dependence of the effect of changing the order of the reaction of the interaction of the components of the foam concrete mixture on the rate constant of the exponential hydration process being established in the form of the technological parameter UP-1 is revealed.
4. A dynamic scheme for controlling the beginning of the process of processes at the boundaries of the phase sections is proposed.
5. The application of kinetic methods of research of technologies for the preparation of foam concrete is justified.

References

1. B.G. Skramtaev, All-Union. scientific-engineering, Builders and Center. scientific-research. in-t prom. Structures (Kharkiv, State.-scientific. tech. publishing House of Ukraine, 1933)
3. V.S. Ramachandran, R.F. Feldman, V.M. Malhotra, etc. (Moscow, Stroyizdat, 1988)
7. S.M. Semenov, Laboratory media for actinomycetes and fungi (Moscow, Agropromizdat, 1990)
8. B.D. Sum, Fundamentals of colloidal chemistry (Moscow, Academy, 2007)
9. B.N. Tarasevich, IR spectra of the main classes of organic compounds: reference materials (Moscow, Lomonosov Moscow State University, 2012)