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CEMENT PASTE AND CONCRETE HARDENING UNDER STRAIN:
I. CEMENT PASTE RESEARCH

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ABSTRACT

This paper describes cement systems (paste, concrete, etc.) hardening under strain (HUS) when those systems get additional strength through adjusted stresses. The fundamental physical and chemical processes and the results of their research are given in the abstract with the mechanism of cement systems HUS.

Introduction

Russia was the first country to conduct research in the field of cement systems HUS as early as the 1930s when work was begun by A.V. Satalkin.(1) Later he published a monograph and a number of articles.(2-4) There are also some other works on concretes(5) and mortar(6) known in the field.

These articles are devoted to research on cement-forced strained-hardening under mechanical loading with the applied force as the early loading. Everyone considered that the reasons for cement hardening under mechanical loading were connected with an extremely easy delivery to the cementing particles in the liquid state as the result of hydrates covering cracking of particles when strained. Cement hardening and other processes under stress were not studied. We ourselves do not know of any work on the problem.

Hardening Under Strain and Conditions for its Appearance

The analysis of the published works(1-6) show that early loading influences the hardening kinetics of water-cement systems. In our work we discovered that the forced strain gives rise to its own strain which is the result of the interior forces' effect appearing in heat exchange processes or phase transition of the first kind. This hardening and melting leads to mutual transitions of water into ice when the system is frozen or heated.

All these facts cause the strain-stressed situation in cement structure. That is why we call the phenomenon of an accelerated increase of strengthening as hardening under strain (HUS). At the same time we consider early loading as a partial cause of this effect.

Cement hardening under strain is the process of acquiring some additional strength by concrete or some other cement system if the hardening process is accompanied by unbalanced strain with a variety of stress meanings. We shall have the process reverse to hardening if these strain meanings are higher, that is the strength will decrease through macro-cracking. The stress admittance may be from 50 to 70% in breaking one, depending on the concrete strength and some other factors.

There are unbalanced processes connected with the unconverted deformation. The converted part of deformation consists of elastic strain and restoring part of creep deformation. Taking this fact into account we may define the unconverted deformation $\sum 1$ as:

$\Sigma 1 = \Sigma 2 - \Sigma 3 + \Sigma 4 + \Sigma 5$, where $\Sigma 2$, $\Sigma 3$, $\Sigma 4$, $\Sigma 5$ correspond to the summary of the creep deformation of a restoring part of the latter, plastic of the second kind and pseudoplastic of deformations.

This expression shows that creep and plastic deformations lie at the bottom of the unbalanced process which is closely connected with concrete hardening. These facts show the influence of loading and atmospheic agents on the process of concrete hardening.

In general, the concentrated aqua-cement systems are in use now. A certain interest may stimulate numerous works on kinetic processes in cement system while hardening with clinker minerals at the base and also on cements with various composition and dispersity with or without chemical admixtures. There are two items rising out of the analysis of these works. First, little attention is paid to the influence of the system deforming on its physical and chemical processes. Second, the above systems have their own natural development. It is expressed by the fact that the curves of the hydrate level of the cement, hydroxyl calcium crystal dimensions, micro-cellular specific surface of cement paste, its porosity, heat radiation and some other characteristics turn suddenly in time after about a 24 hours' hardening at room temperature. This phenomenon speaks of an abrupt slowing of the process of hydration at that time. The curve twists are called extremums.

Such kinetics express a slow reaction between cement and water. In the literature it is explained as the formation of dense surface hydration products on cement grains, that is "skingel." Generally, "cement skingel" is CSH - phase. Some authors believe that cement skingel conserves binding agent particles and prevents them from further hydration. It is believed that a skingel layer does not admit water into the reaction zone and prevents reaction agents from going away. The reason for this effect lies in the high density of the skingel layer.

A traditional explanation of the fact and a gradual density of gel give rise to the question of whether a weak permeability of cement gel is the only reason for a slowing water-cement reaction.

We researched specific electric conductivity time changes of cement paste. The Portland cement paste with normal density consistency test has an increasing display of this characteristic after mixing, but in an hour or hour and a half, it begins to decrease. It is important to note that the low branch of the curve of this dependence begins to slope and coincides in time with an abrupt change. According to the published data the character of the dependence is true for other cement pastes with some other consistency.(7)

Aqua-cement system electrical conductivity affects the transition into the liquid ion phase. The examined dependent curve is identical to the concentration Ca^{2+} time change curve in a liquid phase of cement paste (Figure 1).

The analysis of the data shows that system electrical conductivity is defined by the Ca ion maintenance in a dispersed medium. By the given time their concentration decreases up to the level which does not correspond to the considerable extent of this element in cement. This fact allows one to consider that the liquid state phase (skin water on solid surface) is underestimated from a kinetics process point of view.

Electron microscope research does not prove a high density of hydration products at the early state. While studying tricalcium silicate Portland cement clinker and also some relatively compound

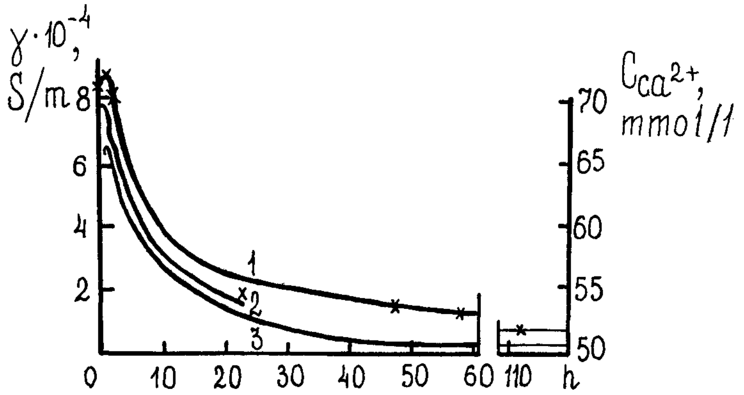

FIG. 1
Changes in time specific electric conductivity of cement paste and contents of calcium ions in the liquid phase: 1, 2 - electric conductivity by the author's data and (7) respectively; 3 - ion calcium contents (8)

mineral mixtures on surface particles of the binding agent, we marked some dendrite interior product blankets which have nothing in common with the dense cover even at 7-day age, as they have a great variety of large hollows.

Such holes in the structure of new particles may serve as waterways into reaction zones because of the small diameter of their molecules (less than 0.3 nm).

But water absorption on hole walls prevents liquid from passing through the skingel of cement paste. The reason for absorption when water passes into the skin state is the abundant surface energy of the hydration products' high dispersed solid phase. At the very beginning of water mixing it is due to cement particles energy.

During the initial stages of mixing water and cement, some hydrates with a large amount of water are formed. Further hydration goes on with a redistribution of a bound water.

The research work of some scientists, that is data from NMR-spectroscope, the passage of hydrosulfate alumina calcium form a tri- to a monosulfate form and some other effects, confirm the above stated as well as the struggle for water mentioned in literature. As a result, old concrete may contain up to 25% (and even more) non-hydrated binding agent core. At the same time their strength exceeds the standard one by 260% at a low rate of hardening.(9)

It is believed that the liquid phase in gel cannot react to non-hydrated cement. This idea corresponds to physico-chemical concepts of water-lost mobility and its dissolving ability thanks to the transition into a skin state.

Therefore, the unhydrated core of a cement grain appears to be covered with a gel having water excess in a bound state. But it is impossible for the water to take part in the hydration process until the liquid is bound with a highly developed surface of hydration products. Some absorption forces help here.

Such an approach is based on a modern point of view concerning the role of the surface forces at the border between solid and liquid phases and leads to two conclusions:

1) The cement hydration process dies away through skingel appearing around the cement particles, but the process is controlled not only by gel density but also by the fact that water binding through interaction with the surface of highly dispersed reaction products;

2) Some technological methods should be used to liberate skin water and involve it in hydration.

One of them is deforming.

The Theory and Mechanism of Cement System Hardening Under Strain

The theory and mechanism of cement-paste-strengthening are worked out on the basis of kinetic conceptions of solid bodies, the chemico-mechanical aspect of the stress-strained state's influence on chemical processes kinetics, polymer interchanges in hardening systems, control for hydration activity and structure formation of cement paste and concrete. The role of liquid phase and hydrogen bonds which lead to the synthesis of non-densed structures with high energy content is taken into account as well.

We stress in our work the positive role of one of the basic physical processes in the theory of hardening and the strengthening mechanism of the stress-strained cement-water systems, that is submicrocracking. This has been observed before but nobody has ever explained the grounds and mechanism of concrete cracking.

The concept of cement-cracking structures having a positive effect at submicro level proves correct if you take into account the dilatone mechanism of breaking and microcracks curing capability in solid bodies.(10)

The formation of embryonic submicrocracks is the first in the group of physico-chemical processes defining hardening kinetics and cement-system-strengthening increase when strained. The above mentioned cracking concentration is from 10^8 up to 10^{17} cm^{-3} despite the nature of solid bodies. Cracks' appearance goes on with dilatone disintegration (density fluctuation) and accumulated energy break, the latter being turned into a sound and heat one, at the end.

Energy evolution during cement paste deformation is being researched in our work with the help of the acoustic emission method. This method allows mark cracking by sound impulse generation. During experiments, impulse amplitude and length as well as quantity are considered. A measurement of amplitude characterizes the size of appearing cracks, whereas a length measurement addresses the energy aspects of the process.

The analysis of cement paste acoustic emission (Figures 2 and 3) results of various aging and curing gives us the opportunity to notice:

1) Embryonic cracks appear independently of concrete aging, curing and hardening conditions at very small strains which are only a small percentage of those breaking;
2) Impulses with high amplitudes are generated at greater strains if cement paste is older;
3) Impulse length decreases with cement paste age;
4) The younger the cement paste is, the greater the number of impulses of acoustic emission are, and the higher the energy dissipation is at a stress range which is optional from HUS point of view;
5) The amount of energy increases as the acoustic component in the emission flow decreases.

Energy dissipation connected with microcracking at deforming is complete when it turns into heat. Heat effects were noticed during experiments not only in cement paste but also in solid bodies from other materials.(10,11)

Taking into account the bursting character of the submicrocracking process dilation mechanism calculated local temperature excursion, the temperatures exceeded average ones of a strained body by ten times or more. This local heat evolution in a great number of microvolumes, according to embryonic cracks' concentration, affects the polycondensation kinetics of new formations in cement paste.

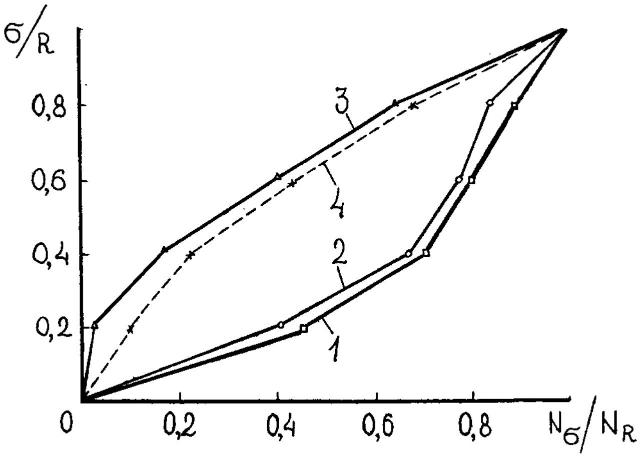

FIG. 2
Dependence between the ratio of the number of acoustic emission impulses at σ and R stress and a relative stress of cement paste hardening under different conditions:
1, 2, 3 - water of 2, 7, 132 days; 4 - air of 132 days

In silicon dioxide agents, polycondensation results in appearing siloxan bonds which leads to dehydration. Released water is able to take part in the reaction. In cement structures, a slow polycondensation process under normal temperatures corresponds to a low rate of strengthening.

This work examines the role of polycondensation effects in hydrate calcium silicates connected with stressed cement paste HUS. Deforming of paste samples formed of synthesized tricalcium silicate and Portland cement clinker was carried out by means of loading and also by freezing and thawing alternately (in accordance with forced and own deformation conditions).

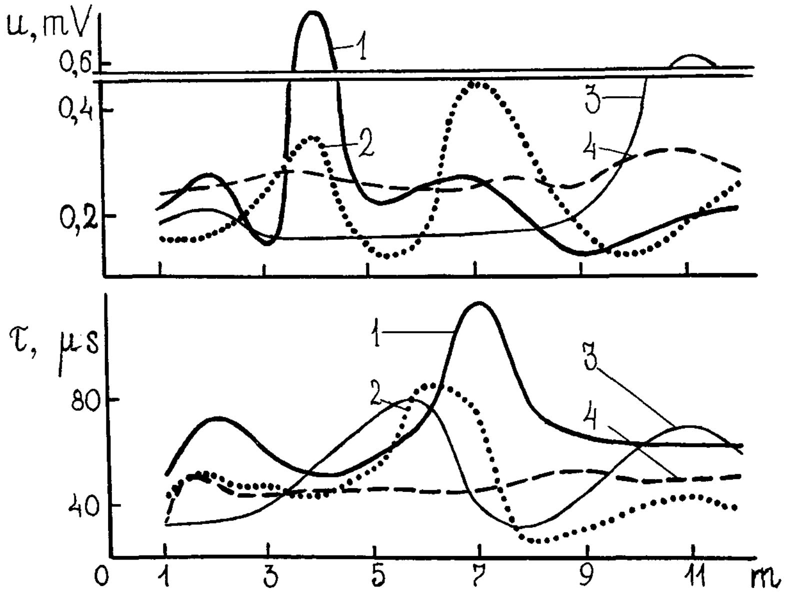

FIG. 3
The amplitude (μ) and length of acoustic emission (τ) signals at different levels of loading (m).
See signs in Fig. 2.

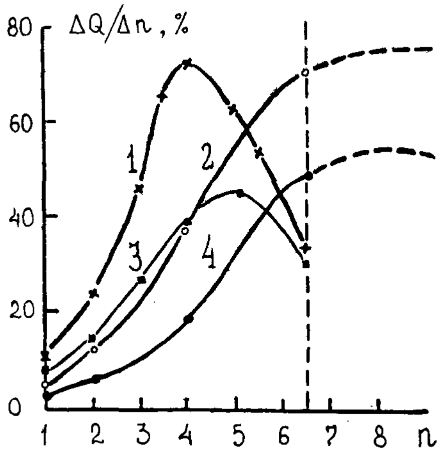

FIG. 4
Mass distribution of calcium hydrosilicates according to a middle degree of condensation for differerent binding agents.
1, 3 - Portland cement clinker and C_3S without deforming;
2, 4 - the same under deforming conditions

Using experimental results, we developed hydrate calcium silicates' mass distribution curves according to the degree of their condensation (Figure 4). We applied the molibdate method here. The results show that despite cement hardening conditions (with or without loading) polycondensation develops from two binding agents contained in the paste. But the system deforming leads to an increase in the degree of condensation of 100%. Bearing in mind data published in the literature, we should state that the effect on deforming polycondensation is like those of chlorocalcium or of increased temperature. In all these cases, along with the increase in the degree of condensation, is an accelerated increase in the cement paste strength.

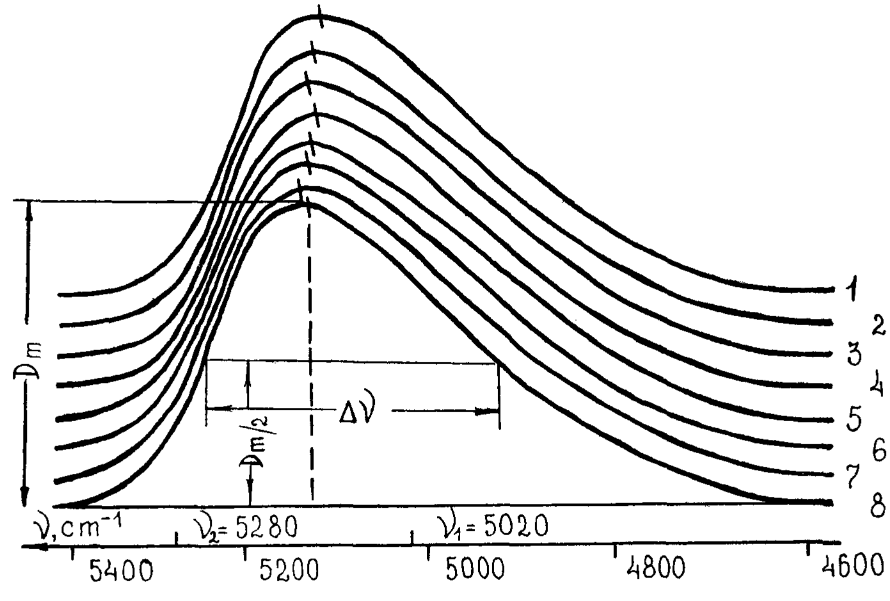

FIG. 5
Infra-red spectroscoping. Valency - deformation stripes of involvement near the frequency of 5180 cm^{-1} of mixing water agents: 1 to 4 - running water; 5 to 8 - melted snow water;
1, 5 - water without admixtures; 2, 6 - water + Portland cement; 3, 7 - water + perlit powder;
4, 8 - water + air involving admixture; the contents of all admixtures is 1% from water mass;
υ - frequency of involving stripe maximum; Δυ - half-width of invovling stripe;
Dm - optical density

Such polycondensation kinetics is connected with the accelerated recoiling of water with the latter being involved in hydration. Besides there may be some released water during thermodestruction of ettringite.

Recoiled water (like that in the concrete mixture) changes its structure due to the effect of temperature, which, in turn, is connected with a local rise of temperature during the deforming process. Absorption of outer heat and the effect of some dissolved agents also affect the structure of water, which is defined by the geometry and energy of hydrogen bonds. The results received during the experiments with mixing water agents carried out with the use of chemical microrhelogical and infra-red spectroscope methods confirm this fact. Studying various spectral parameters, a sheared elastic strain hydrogen index and ion composition of mixing water agents (Figures 5 and 6; Table), shows that temperature changing chemical admixtures, and some other factors which affect the strength of the system, have a positive influence on the composition, structure and reaction ability of water.

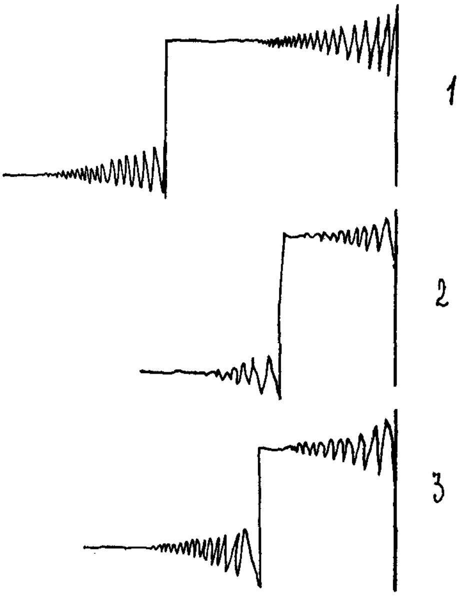

FIG. 6
Curves of sheared elastic deformation of water:
1 - running water; 2 - melted snow water;
3 - distilled water

TABLE
Hydrogen index and ion composition of water in mg - eq/1
(tested at 20° C)

Characteristic of Water	PH	Ca^{2+}	Mg^{2+}	Na^{+} K^{+}	Cl^{-}	$CO4^{2-}$	$HCO^{-}3$
Running	9.4	0.90	0.60	13.3	0.9	13.0	1.0
Melted Snow:							
Fresh	10.4	0.45	0.05	7.7	1.0	4.5	1.9
Heated up to 70°C	11.8	0.39	0.06	6.8	0.7	4.0	1.7
Kept for 3 days	11.6	0.70	0.20	7.5	0.5	4.0	3.7

Elastic shear deformation curves of water vary greatly from one to another if we consider running water, melted snow water or distilled water. This fact corresponds to their different compositions and structural peculiarities. The date received during experiments allow us to see that the role of water in hardening cement systems is more significant than it was believed to have been before. It is defined by the hydrogen bonds' energy giving to the liquid this or that structure.(12,13)

The liquid phase of the deformed cement system, including the water released during polycondensation of hydrated calcium silicates and ettringite thermodestruction, is activated. Additionally the water is subjected to thermoosmosis, which is confirmed by the results of silicate structures research.(14) As a result of diffusion, mass transference increased during hydration hardening.

The study of interior stresses in cement systems showed that numerous faults inherent in them play the role of stress concentrators. While deforming interior stresses relax, cracking occurs in the zone of faults. Cracks are the method of cement hydration products' transference into such zones. At first the pre-existing faults are cured by these products; further new cracks are treated in the same way. In the end, this process results in the leveling off of the density stated before, as well as HUS.

All the examined physico-chemical processes constitute the basis for the deformation theory of cement paste strengthening.

In the deformed samples (D-samples), owing to the above-mentioned processes, hydration takes place more intensively than in non-deformed ones (n-samples). This effect has been defined with the help of a number of physico-chemical methods.

The results of NMR - spectroscope examination based on high proton emission show that the semiwidth of the D-samples lines of absorption is greater than that of N-samples made both of tricalcium- and ß-dicalcium silicates (especially of C_3S). This fact speaks of a closer bond of hydrated water.

According to the data of thermogravimetric analysis, D-samples, in comparison with N-samples, lose more mass (the difference is up to 20%), have more chemically bound water and greater intensity of heat effects at 140-150°C; that, in turn, proves a higher content of chemically bound water and portlandite phases.

Roentgen phase analysis shows that D-samples, in comparison with N-samples, have less intensity of clinker phase peaks (0.263; 0.279; 0.289 nm lines and some others), but they have more peak intensity of hydrate phases (0.181; 0.193; 0.497nm). Hydrate phase lines 0.326 and 0.426 nm are not available for the N-samples, which also shows an increased hydration under deforming conditions.

The same conclusion appears from the data for the specific surface of hydrated samples.

Our results prove the intensification of cement hydration under the conditions of its own strains, as well as the trustworthiness of conceptions about the mechanism HUS.(15)

Summary

An embryonic (starting) submicrocracking lies at the bottom of strains HUS mechanism of cement systems. The submicrocracks are marked early as negligible deformations corresponding to very small stresses. Conceptions about the delatone mechanisms of solid bodies' destruction, cement structures being among them, testify to the fact that submicrocracks' appearance is accompanied by a considerable local increase in temperature in a great number of points of the system. Under these conditions, polycondensation processes are intensified. The latter leads to

accelerated water release, the water being necessary for the hydration of cement in the system. During polymer conversions this water is not only released but also activated. The reasons for water activation are numerous, but one of the most important in this case is heat influence, which follows, consequently, local temperatures increase while deforming. Temperature gradients connected with them provide a thermoosmosis flow of liquid into reaction zones and lead to the appearance and acceleration of diffusion and relaxation effects. Operations of this mechanism result in accelerated hydration of structure formation and increased strength of deformed cement systems.

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References

1. Physical-Mechanical Properties of Concrete, Leningrad-Moscow, pp. 48-67 (1939)
2. Satalkin, A.V., B.A. Senchenko, “Early Loading Concrete and Reinforced Concrete,” in Bridge-Building, Moscow (1956)
3. Transactions of Conference by Chemistry of Cement, Moscow, pp. 154-172 (1956).
4. 6th Leningrad Conference by Concrete and Reinforced Concrete: Reports, Leningrad, pp. 133-140 (1971)
5. Gorochov, V.V., Defects of Hydrotechnical Concrete Structure, Moscow-Leningrad (1965).
6. Building Materials,6 28-29 (1955).
7. Babushkin, V.I., Physical-Mechanical Corrosion Processes of Concrete and Reinforced Concrete, Moscow (1978).
8. Technology and Durability of Reinforced Concrete Constructions, Moscow, pp. 143-150 (1983)
9. Pulatov, Z.P., U.P. Inozemtser and N.A. Sirasiddinov, Cements for Massive Concrete Constructions, Tashkent (1984).
10. Physics of Strength and Plasticity, Leningrad (1986).
11. Hydrogen Bond, Moscow (1981).
12. Physical Chemistry, Modern Problems, Annual Report, Moscow, pp. 6-40 (1984).
13. Chemistry and Technology of Water, 4 (6), pp. 485-494 (1982).
14. Derjaqin, B.V., N.V. Churaev, V.M. Mooler, Surface Forces, Moscow (1985).
15. Rahman, A.A. and D.D. Double, Cement and Concrete Research 12, (1), 33-38 (1982).