Non-Markovian processes in cement systems

Yu S Sarkisov¹, L B Naumova², N P Gorlenko¹ and N N Debelova¹

¹Tomsk State University of Architecture and Building, 2, Solyanaya Sq., 634003, Tomsk, Russia
²Tomsk State University, 36, Lenina Avenue, 634050, Tomsk, Russia

E-mail: sarkisov@tsuab.ru

Abstract. Non-Markovian processes occur in nature in the form of the structural organization laws of space-time objects at different scale levels. Non-Markovian processes preserve the memory of the past state of the system, and its further evolution is largely predetermined by information about previous stages of development. This is typical for solid-phase processes, ceramics, metals and alloys, water and aqueous solutions, and other inorganic objects. Non-Markovian process indicators are the natural harmony numbers, Fibonacci numbers and golden ratio. The paper presents evidence of non-Markovian process occurred in cement systems. It is shown that during the formation of the fine-grained crystalline structure the cement system is capable to produce such elements and generate a low-frequency current, which simulates the intensity and duration of the processes. It is shown that the active phase of self-organization in cement systems is of temporary nature as the energy from outside sources is limited.

1. Introduction

To date, the world science has accumulated a large bulk of theoretical and experimental data that are a basis for confidence that the formation of the new natural science paradigm takes place [1]. The latest achievements in physics, chemistry, biology, ecology, economics, social sciences, cybernetics, synergetics, management theory and other sciences lead to understanding of a deep correlation and unity of processes, which occur at micro-, macro- and mega-levels, and to hierarchy of structural levels, organization of material objects of organic and inorganic nature [2].

According to the concept of the phenomena unity in nature, the behavior of any object or the specified system of objects in the Universe is determined not only by their internal but also the external structure and properties of the environment in which they exist and by the number and quality of interactions between them. This law formulated by Carl Rouillier, the Russian scientist, states that the results of the development (changes) of any object (organism) are determined by the ratio between its internal properties and the properties of the environment in which it exists [3]. This applies to both organic and inorganic systems and completely corresponds to the universal ecological paradigm [4].

Each object interaction between each other and the environment that repeats many times, leads to the accumulation of responses to an external impact, restructuring of elements, adaptation, weakening of the negative external forces for the preservation of the whole and, conversely, strengthening of positive functions that increase the stability (self-preservation) of the whole. This is pertinent particularly in living species, all the more intellectual at a valuable knowledge selection and assimilation and a rejection of useless information or noise. The development and evolution of systems, both based on memory of the past state are called non-Markovian processes, unlike the Markovian ones, for which the memory of the past is less significant [5].
If the memory of sentient beings does not cause special discussions, the memory of inorganic objects is sometimes simply ignored [6]. In the authors’ opinion, this is deeply wrong, because one cannot deny the ability of any system to return to its original state after any external influence. The dynamic stability and relaxation are impossible without the memory phenomenon. The memory of multicomponent collective systems is much more perfect than the individual one, which means that collective systems possess an increased dynamic stability and durability [7]. Memory processes are typical for any objects of inorganic nature, both for metals, alloys and silicate, refractory nonmetallic systems, and for water in particular.

Currently, there is no doubt that not only the origin of a given object and the nature of chemical bonds composing its structure, but also its biography (the history of preparation for relations with other objects and the environment) determine its reactivity.

The thermal, mechanical, chemical, and biological history of the material as well as the known shape memory effect [8], are inextricably linked with the structure of a solid. Modern material science, including science of construction materials are based on this concept.

In general, the effects associated with the data mining, storage and communication are widespread in inorganic matter. Any complex system (condensed matter) has a hierarchical multilevel structure. At present, the structural levels of the solid organization are distinguished as crystallographic, fine-grained crystalline and rheological. At the same time, the fine-grained crystalline structure is crucial and determines the ability of the system to self-organization [9].

The effects of top chemical memory, their nature and role in the synthesis of solid-phase substances and materials are described by West in [10]. He notes that between two limit states, that match a complete aggregation and disaggregation of the elementary volumes of the system, an infinite number of real structures probably exists, which is characterized by different degrees of aggregation (both in size of aggregates and in binding energy of individual elementary volumes of the system in these aggregates). This implies the existence of a huge number of intermediate metastable states or a metastable diversity [10], which is the most important condition for the sustainable system existence. According to the Soroko theory [11], the system in its development always chooses the path of the maximum implementation of its possible states.

The above considered effects are typical for polymers also. For example, Kozlov [12,13] shows that the structural memory of the polarylate macromolecular coil is based on the fractal mechanism. Fractals can exist only as a result of the non-Markovian process. Of course, the memory is also characteristic of water in any aggregate state. Water, as a sensor of weak and even very weak external impacts of physical and chemical nature [14], has attracted much attention from scientists. This is because water, as a sensor, can be easily subjected to various processing techniques and, consequently, its reactivity can be controlled. Many Russian and foreign scientists experimentally proved that the processed water is able to preserve the acquired properties for a relatively long time, i.e. from several minutes and hours to several years. It is enough to point out the properties of holy water.

Undoubtedly, the water memory effect is also connected with its structure, or to be more precise, with the variety of metastable states mentioned above. However, the technical difficulties existing up to now, in recording the instantaneous changes in liquid water and water solutions cause fierce disputes from unconditional recognition to absolute negation. But a combination of physical, chemical, geological, biological and other properties of water, which are largely anomalous by nature, make it impossible to negate the water structure. And with the development of terahertz (and higher) spectroscopy [15], we believe that this problem will be solved in the near future.

For many years, the Russian scientists and the authors of this work, have proven theoretically and experimentally the ability of water to the information interaction with the environment [16–26]. The problem of the microwave radiation which provides the information influence on water is described in [19].

The information influence can be described as an energy which is much less than the energy of thermal motion \((kT)\) which is about 2.48 kJ/mol. In the cement-water system, such interactions manifest themselves to the full extent.
In our early research [20] we show that solidification of the cementitious matter is an evolutionary process of the kinetic phase transformation to a dispersion system, during which the initial dispersion medium transfers to an internal phase, and *vice versa*. As a result of complex physicochemical processes, various structures gradually change, such that the higher-order structures emerge from the lower-order structures. The more perfect crystal structure forms *via* the destruction of the previous coagulation structure. Thus, the formation of new structures is, at first, of the destructive nature, *i.e.* the new coalescing contacts emerge after the destruction of old ones. Destructive phenomena in the cementitious matter are accompanied by the formation of the dissipative structures. Each new stage of the structural rearrangement of the cementitious matter can be considered as a nucleus of its further evolution driven by the equilibrium-nonequilibrium factor [21]. The formation of each subsequent phase is a pattern determined by the accumulation of chemical structure-forming agents in the volume of inter-particle contacts due to dissolution of the initial or preceding phase. The conditions for self-organizing hierarchical structure gradually appear in the system. Self-organization is accompanied by a decrease in symmetry of structures, since each subsequent structure has a more complex organization than the previous. The symmetry violation is a kinetic phase transition, and in these terms, solidification of the cementitious matter can be considered as a total phase transition. Obviously, the observed phenomena occur due to changes in the symmetry of hydrated newgrowths. Depending on the specific conditions, a succession of minerals and phases with which water is in non-equilibrium, varies during the relatively long-term structure formation. Metastable particles are substituted by new-phase particles, more equilibrium relative to water. The composition of the newgrowths may differ significantly from the initial cement grains and depends on the nature and conditions in the cement-water system.

The variety of chemical reactions of the initial cementitious matter with water determines the secondary phase formation and stages of the ongoing processes. The case is that the new phase formation inevitably leads to a change in physicochemical properties of the medium, which, being in higher equilibrium with this or that phase, may turn to be in non-equilibrium with it and become the source of another phase formation. It should be noted that neither water nor cementitious matter determines the structure of hydrated cement. This structure results from the interaction between the solid and liquid phases, its harmony is achieved by an oversaturated solution. The variety of the solid-phase material composition provides the conditions under which water and the resulting aqueous salt solution will be in equilibrium with one group of minerals or individual system components and in non-equilibrium with another group of solid-phase particles. These processes are of an autocatalytic nature. At this stage, the hydrate newgrowths are described by a drastic increase in concentration of secondary active centers. The concentration of primary centers lowers, as the layers with the least structural disturbance are continuously exposed, while the surface layers react with water. The formed primary hydrate phases usually have an amorphous and unbalanced structure, which leads to an increase in the concentration of secondary active centers, which induce oscillations called pacemakers. They usually occur at the interface between the solid and liquid phases and cause the surface defects the behave as chemically active centers. Competition between such centers makes the pacemaker, which generates waves with the maximum frequency, to suppress all other centers. Therefore, a kind of selection of active surface centers occurs in the cementitious matter at the stage of the dissipative structure. The rhythmic formation of secondary hydrates reflects the ability of the cementitious matter to reproduce similar structures. The structural reproduction is one of the most fundamental properties of self-organizing systems. According to [22, 23], one of the possible reasons for this reproduction is rhythmicity of external electromagnetic influence or the ability of the system to generate such fields and radiation at a certain development stage. The generation of an electric signal in water exposed to the laser radiation [24] or the generation of natural low-frequency vibrations in the cement-water system [25] can serve here as examples.

Self-organization of the cement systems is based on their ability to reproduce similar structures at the stage of fine-grained crystalline structure formation.
During the dispersion of the new phase to colloidal and nanoscale, the system is able to generate low-frequency current, which may serve as a source of the coded data on the reproduction of similar structures. The structure reproduction runs, probably, by the fractal mechanism and corresponds to Zipf's law [26] and must be somehow connected with the parameters of the golden ratio and the Fibonacci numbers [27, 28]. This means that the external electromagnetic field imposition can change the conditions of the structure selection and lead to the formation of hydrated cement with properties differing from those created without the external influence. In a number of cases, the structure reproduction can occur by the well-known Feigenbaum scenario [29], which in stable systems has a rhythmic oscillation character in contrast to systems aiming to chaos and destruction, with the continuous oscillation spectrum.

It is known that the induction periods of hydration and structure formation are interconnected processes and conditioned by the transfer mechanism and nature of hereditary characteristics from oversaturated solutions to the future hydrated cement structure. Unfortunately, it is still not clear how this process occurs.

Up-to-date theories of nucleation cannot yet explain why crystals sometimes do not grow even in oversaturated solutions; why the growth rate of the same crystal side fluctuates in time; why the impurity content of one and the same crystal varies by dozens of times, etc. The works [30, 31] show that the time required for the nucleus growth up to critical size is incomparably longer than the time of formation of crystallization centers. Hence, the beginning of the pre-critical stage limits the formation process of critical nuclei. Thus, in water crystallizing, the nucleus growth up to three or four particles requires more than 90% of the time required for the critical nucleus formation.

In the authors’ opinion, the particles of the new phase are considered to be in the excited state relative to the oversaturated matrix of the solution components, which, in turn, are excited relative to the dissolved components, while the latter are excited relative to the initial components. Then, the transition from the nonexcited (main) to excited state can be simulated with a certain approximation as a quantum transition from one energy state to another.

Haken [32] reported that near the generation points of the new phase, all information was in the nuclei rather than in the oversaturated solution matrix. He proposed a hypothesis that a stage-by-stage transfer of hereditary characteristics occurred from the initial to dissolved particles, from the latter to hydrates, and from the oversaturated solution as a whole to the hydrated cement structure. By regulating the level of excitation energy from outside, especially at the earliest stages of the structure formation, it was possible to control not only the time of crystallization processes, but also the spatial parameters of the future structure.

Undoubtedly, the problem raised is extremely complicated and requires an in-depth and comprehensive study. We consider the solution of this problem to be impossible without clarifying the role of the cooperative phenomena in the structure formation of dispersion systems. The cooperative behavior of the system can take place only far from the equilibrium state, when the interaction between the particles is informational in nature. As is mentioned above, the information readout and coordination begin at a stage of the structure translation. Then the structural information of a solid occurs in spiral order, from the surface to the bulk crystal; for water is occurs in the opposite direction. As a result, a saturated solution is formed, which is the information storage about the future structure of hydrated cement. It is the saturated solution that controls the evolution of the cement-water system. However, during the new phase generation, all information is already in the carrier elements of the future structure of hydrated cement. We would like to note once again that neither water nor cement determines the hydrated cement structure. The latter is the product of the actions of both "parents", whose harmony is achieved in the oversaturated solution. For this reason, the variety of structural elements saturating the solution, and the degree of its structuring are the source of generation of new information from which a new phase crystallizes. The forming solution is constantly in non-equilibrium or metastable state or to be more precise, in the state of transition from one metastable state to another. This continues until the excitation sources of the equilibrium state exist. However, unlike the geological or biological structures, the solution cannot continuously saturate after its next
removal. In artificial curing systems, dissipation manifests itself only in a limited period of time. In natural objects dissipation occurs during a relatively long time and has a periodic, rhythmic character. This is because the abundance of negative entropy sources [33] in natural objects exceeds the self-organization ability of artificial systems, including the cementitious matter.

Any information process indicators are the natural harmony numbers, golden ratio, and Fibonacci numbers [34], which help to control and correct the hydration and structure formation processes of hydrated cement as well as to create structures with the specified set of properties, and then develop a generation of new building materials on their basis.

References
[1] 2001 Philosophy of science. Formation of the modern natural science paradigm p 270
[2] Shcherbakov A S 1990 Self-organization of matter in inorganic nature. Philosophical aspects in synergy (Moscow: MSU) p 105
[3] Roulier C F 1954 Selected papers on biology (Moscow: USSR Academy of Sciences) p 78
[4] Krushakova A A 2001 Philosophy of science. Formation of the modern natural science paradigm 7 124
[5] Shelepin L A 2001 Philosophy of science. Formation of the modern natural science paradigm 7 24
[6] Knazyeva E N, Kurdyumov S P 2016 Filosofiya i sinergetika 6
[7] Dobrocheev O V 1995 Mendeleev Chemistry Journal 39(2) 48
[8] Oleinikov N N 1995 Mendeleev Chemistry Journal 39(2) 86
[9] Legasov V A, Oleinikov N N, Tret'yakov Yu D 1986 Russian Journal of Inorganic Chemistry 31(7) 1637
[10] West A R 1998 Solid State Chemistry and Its Applications. Pt I (Moscow: Mir) p 555
[11] Soroko E M 1984 Structural harmony of systems (Minsk: Nauka i tekhnika) p 264
[12] Kozlov G V 2007 Proc. 17th Mendeleev Forum on General and Applied Chemistry Moscow 175
[13] Dorozhkin K V, Dunaevsky G E, Sarkisov S Yu, Suslyayev V I, Tolbanov O P, Zhuravlev V A, Sarkisov Yu S, Kuznetsov V I, Moseenkov S I, Semikolenova N V, Zakharov V A, Atuchin V V 2020 Mater. Res. Express 4 1062011 doi.org/10.1088/2053-1591/aa8f06
[14] Lobyshev V I 2007 Mendeleev Chemistry Journal 11(1) 107
[15] Shandako S D, Kosobutskii A V, Sevast'yanov O G., Lomakin M V, Sarkisov Yu S, Sarkisov D Yu 2016 Russian Physics Journal 59(5) 130
[16] Naumova L B, Gorlenko N P, Kurzina I 2018 Environments 5(1) 16 doi:10.3390/environments5010016
[17] Aksenov S I 2004 Water and its role in regulation of biological processes (Moskva-Izhevsk: Institut komp'yuternyh issledovanii) p 212
[18] Naumova L B, Minakova T S, Gorlenko N P, Kurzina I A, Vasenina I A 2018 Environments 5(7) 82 doi.org/10.3390/environments5070082
[19] Gorlenko N P, Yu S Sarkisov, Syryamkin V I, Naumova L B, Pavlova A N, Laptev B I 2019 IOP Conference Series: Materials Science and Engineering 597 012030 doi:10.1088/1757-899X/597/1/012030
[20] Levdiyova T L, Tsyganyuk Yu I, Sarkisov Yu S, Gorlenko N P, Dunaevskii G E 2003 News of Higher Educational Institutions. Construction 11 51
[21] Sarkisov Yu S, Kuznetsova T V 2009 Tekhnika i tekhnologiya silikatov 4 2
[22] Zhavoronkov M M, Nekhoroshev A V, Gusev B V 1983 Proc. USSR Academy of Sciences 270(1) 114
[23] Smirnov A N 2000 Mendeleev Chemistry Journal 3 29
[24] Andreev A N, Kulevskii L A 2008 Applied Physics 4 30
[25] Gorlenko N P, Sarkisov Yu S, Kuznetsova T V 2004 Tekhnika i tekhnologiya silikatov 1 14
[26] Barkevich S Ya 1993 Cellular automation as real model of new ideas on physical and
information processes (Moscow: MSU) p 112

[27] Shipitsyn E V, Popkov V V 2001 Vestnik mezdunarodnogo instituta Bogdanova 7
www.ephes.ru

[28] Klyuikov S F 1997 Numbers and knowledge of the world (Mariupol': InformMenyu) p 112

[29] Feigenbaum M 1983 Physics – Uspekhi 41(2) 343

[30] Belintsev B N 1989 Priroda 2 81

[31] Petrovskii V A 1983 Mendeleev Chemistry Journal 57(8) 2575

[32] Haken H 1980 Synergetics (Moscow: Mir) p 404

[33] Rebane K K 1985 Energy, entropy, environment (Moscow: Znanie) p 64

[34] Ol'chak A S 2009 Natural and Technical Sciences 2 19