

# Theory of polystructural properties of silica-lime construction materials

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**Abstract.** During construction of low-cost residential housing, it is necessary to use local raw materials, to increase the variety of manufactured products and to implement energy-saving technologies. Such technologies include, in particular, the contact-condensation (non-autoclave) technology created by V.D. Glukhovskiy and R.F. Runova. According to it, non-stable calcium hydrosilicates are produced in an isothermal reactor – a batch crystallization vessel. Then they are mixed with fine filler until attaining the moulding water content; the raw goods are compacted at the increased pressure and dried. After pressing water-resistant wares of sufficient strength are formed. The technology for separate hydrosilicate production with their further compacting considerably expands the subset of control actions over system as compared to the traditional autoclave process. The study of mutual coordination and kinetics of the composite frame formation and its probable structure simulation are among the list studied field in material science. Some scientists defined this problem as the most difficult in material science and considered implementation of theoretical modelling (replacing a real object with its analogue) as a way of its successful resolution. We make a conclusion that the examination of polystructural properties would adjust us to forecast a further development of silica-lime products.

## 1. Introduction

Contact-condensation technology is not widely used yet to fabricate silicate products. Basically, it is due to rheological features, namely, handling highly-dispersive systems. Undesired coagulation phenomena complicate the technology and decrease contact condensation efficiency. Overcoming difficulties due to the higher water-solid ratio requires the higher energy consumption to remove excessive fluid while mixing the components enhances coagulation phenomena.

“Self-drying” was used to bring the system moisture content to the moulding value by mixing the binder with fine filler, which removed excessive moisture. However, this process results in the non-uniform distribution of the binding agent over filler grains due to increasing surface tension on the aggregate and the continuity fracturing.

It is known that the system continuity fractures yet at moisture content of 20% to 25%. Application of surfactants may solve this problem to some extent. Partially, the problem may be solved by identifying determinative cluster structures and their simulation. It allows identification of control actions per each sub-model while the plurality of such sub-models will define the range of compromise among them (taking into account the interfacing boundary conditions). Besides, the



dedicated papers do not properly describe the contact technology mechanism itself that makes it difficult to estimate the impact of input control actions on the process efficiency.

Contact-condensation technology may be attributed to a complicated system. Decomposition method permits to divide it into simpler technological operators and to formulate a mathematical model per each operator with further linking input/output parameters. Also, a subset of efficiency criteria should be formulated per each sub-model with their inter-linking by hierarchy. Meanwhile, it is difficult to use the criteria proposed by V.D. Glukhovskiy and R.F. Runova to estimate the material trend to contact condensation since they are not related to process parameters. Significant experiment results were accumulated in the study of the silicate (silica-lime) system pressing; however, theoretical justification and simulation are limited by several specific features:

- The system contains several inter-dependent phases;
- The inter-relation between subsets of structural and parametric indicators during the silicate system evolution;
- The formation of a variety of intermediate meta-stable phases in the system with different re-crystallization periods;
- The availability of positive and negative feedback in the evolving system that considerably affect kinetic processes;
- The cooperative and threshold phenomena for different phases in the system, which multiply with increase of dispersion degree, etc.

This paper presents a theoretical study of the influence of the formation of interparticle contacts according to the hierarchical principle of polystructure.

The following factors may serve as the reserve to increase the strength of coagulating systems: decrease of particle diameters and increase of their concentration, transfer of macropores in micro- and ultra-pores, attaining the limit packing degree due to force actions. The use of theoretical modelling is justified in relation to the knowledge of complex building materials, mixtures, objects, etc. This approach allows establishing signs of the subject being studied, which previously not known and therefore not explained.

## 2. Methods and mechanisms of action

Thus, based on the above mentioned aspects, it should be noted that, contact-condensation technology is an efficient way to solve the set task. It is based on the separate technology idea when the unstable component is prepared separately.

The role of compacting pressure is reduced to move contacting particles into the area of the nearest potential well, where irreversible water-resistant phase contacts will appear.

The following factors are necessary to implement this technology:

- Availability of unstable particles, which may be prepared using a chemical reaction in crystallization reactors;
- Binding of said particles to produce a water-resistant phase contact by compacting, fluid syneresis or other method.

V.D. Glukhovskiy and R.F. Runova have worked out a classification of silicate materials in unstable state, studied condensation properties of certain materials both in aqueous and non-aqueous condition, their ability to form water-resistant phase contacts, etc.

Pycnometric (true) density, condensation heat, dielectric permittivity, etc. were selected as indicators that feature the contact-condensation ability.

It was mentioned that condensation is considered as a result of the work performed by surface electromagnetic forces to displace macro particles of  $> 10^{-6}$  cm. The following phenomena were taken as distinctive features of the unstable material aggregation:

- No change in chemical composition and processes at the ion-molecular level;
- No substance dispersion into molecules;

- No displacement of particle material macro volumes;
- No thermal energy supply.

Thus, these specific process features made possible to consider aggregation of unstable materials as a specific condensation type – contact condensation, which is chemical bonding between particles bypassing different intermediate forms.

It should be noted that many researchers doubt the crystal lattice coincidence, smoothness of atomic surfaces when forming phase contacts. It follows that intermediate structures should be involved to form the necessary area of inter-particle phase contacts [1].

### 3. Results

The theory of polystructural properties arises from the system polydispersity. Monodispersity condition usually accepted in mathematical models does not result in coagulation and system structuring.

To compact the lower-level structure, it is necessary to re-arrange the higher-level structure at first. For example, the arched structure effect during deformation of powder materials complicates compaction of finer formations inside the arch; and additional energy of activation – vibration is necessary to decrease it. The impact on lower-level structures in the hierarchy may be carried out in heterogeneous medium and through other phases.

Crystals grown in a crystallization reactor have a certain range of the size distribution density and feature meta-stable phases; that is why they will have different ability to coupling. Crystals with higher crystallinity will feature the lower condensation probability. The system with the separately prepared binder will contain the undissolved phase particles as well as other formations with different electrokinetic potentials.

### 4. Discussion

The macroscopic theory of molecular interactions for condensing bodies was developed by E.M. Lifshitz et. al. [2] taking into account the wedge force effect.

Complete coalescence is typical for particles with low surface tension and high kinetic energy of the components capable to overcome energy barrier. Obviously, re-crystallization considered by some authors as a special coalescence type (due to particle dissolving up to critical size) does not also comply with our analysis.

Several researchers [3] observed the formation of lamellar structures in gel systems; however, the mechanism and range of the forces acting in them were not clear. Later researches only revealed the density change along radius in such cluster structures.

The theory of the colloidal system stability by assessing disjoining pressure allows answering the question: in what direction and with what intensity will the aggregation process advance. However, it does not explain, how the synthesis will occur.

The answer may be found using the V.I. Solomatov's theory of the system polystructural properties [4, 5]. According to it, each inter-boundary zone between the structure-forming elements is considered as the contribution by boundary zones with a lower hierarchy level with the corresponding set of structural components.

Evaluation of different mechanisms for particle interaction during incomplete coalescence shows that phase contacts appear by filling the structures with a higher hierarchy level. According to A.F. Polak, in the crystallization theory a seed may appear in the gap between bigger particles if its size is critical. However, M.M. Sychev noted as invalid to apply thermodynamics laws to such dimensions and interpreted the known experiments performed by E.D. Shchukin et. al. [6, 7] as chemical linking of surface valence bonds. Thus, chemical linking will occur for small distances, or the gap will be filled with lower-level structures.

A.V. Volzhenskiy, P.A. Rebinder, A.A. Paschenko et al. associated appearance of irreversible phase contacts in the crystallization theory with gel phase films.

M.M. Sychev, D.I. Stackelberg et al. believe that contact interactions are the basis for any kind of structural transformations: crystallization, polymerization, coagulation, etc. Due to the energy unsaturation of contacting surfaces, 2D areas with peculiar properties form in the contact zone.

P.A. Rebinder defined bonds in gel phase as thermodynamically unstable that should re-crystallize.

Some researchers (P.A. Rebinder, O.P. Mchedlov-Petrosyan, M.M. Sychev et. al.) consider hydrosilicates as inorganic polymers, which structure forms due to polymerization of silica acid anionic complexes. According to R.K. Iler, aggregation results in formation of a fibre form and is performed according to the scheme: monomer  $\Rightarrow$  dimer  $\Rightarrow$  oligomer  $\Rightarrow$  particle.

Surface silanol groups SiOH are replaced by siloxane bonds Si-O-Si in both processes, i.e., on molecular and meso-levels. Fine particles ( $< 3$  nm) are coupled in unstable chain segments, which transform later into spatial 3D structures.

The bridge between contacting particles is formed by the mechanism proposed by F.W. Ostwald, H.M.F. Freundlich, R.K. Iler (solubility vs. particle radius). The contacting surface is considered as a plurality of positive and negative curvature radii with different solubility. In the point of the spherical particle contact, negative curvature radius and solubility tend to zero resulting in immediate monomer precipitation. Then, siloxane binding takes place.

R.K. Iler admits another condensation scheme: the sol thin film dries so quick that a gel net does not have time to form; and a more dense packing structure forms comprising sol particles. Condensation of such film forms more robust structure that will not shrink later. This idea is especially interesting regarding the processes occurred in thin heterogeneous films between structural elements.

Some researches believe that high amorphization during the binder solidification makes diffusion processes quite feasible.

According to J.I. Frenkel's theory, the solidification process is caused by an excessive concentration of vacancies appeared in the border layer due to its curvature and broken bonds and, in this connection, the appearance of their irreversible displacement to free surfaces (discharges). Material grains simultaneously move into the border zone and form a transition area on its basis. Diffusion may occur in surface layers or through dispersing fluid. The particle flow increases the area of phase contacts in contacting particles. Aquacomplexes, associates, weak hydrogen bonds may also serve as bridges (so-called "links") between grains; during aggregation, the first ones will decrease their entropy due to re-packing and further closing while the second ones will be replaced by stronger bonds.

The decrease of the phase contact area is accompanied by entropy decrease. The structural disorder area features gradients of chemical, temperature potential and appearance of flows with different properties due to them. Inter-particle structures are formed according to the hierarchic principle of polystructural properties formulated by V.I. Solomatov [4]: "structure in a structure", from top downward to ion-molecular level based on the least energy principles. At the same time, forces with different values and caused by different structural units form inter-particle structures. This principle will be observed in contact-condensation technology; however, activation energy allows excluding certain bonds from the intermediate structure chain, for example, weak hydrogen bonds. Process dynamics will be defined by the bond formation time and outer impact  $X(t)$ . The effect of poly-structural properties of boundary areas will increase with the increase of aggregating particles. Intermediate inter-boundary areas serve as transfer members of the power chain (from top to bottom) for the particles forming the irreversible phase contact. Dispersing medium will partially execute these functions; it is not only a lubricant but also it forms hydrogen bonds, recombines the structure affected by hydrodynamic gradients. In this way the contact-condensation ability was the most efficient for gel-type and sub-microcrystalline particles, elementary crystallites.

## 5. Conclusion

Thus, the Review of the papers dedicated to the simulation of structuring processes in construction materials showed that most models were based on the complex of linear and non-linear regression dependencies obtained during search works and statistical data processing. However, their information

content of the models decreased since they were obtained for particular objects within the narrow time and space ranges; therefore, it is difficult to extend them over similar phenomena.

A.F. Polak demonstrated that solidification was connected with the transfer of coagulation contacts between particles into crystallizing ones and was due to the appearance and growth of 2D seeds in the gap between substrates, which was more beneficial in energy sense as in the solution [8].

During the seed growth, adsorbed molecules permanently diffuse in the gap. This energy relation enables obtaining the expression that connects crystallization time, solution oversaturation degree, particle sizes, and the distance between them. By setting three out of four parameters, it is possible to obtain critical values for the remained one, at which particles may coalesce.

In our opinion [1], the model of the silicate mixture compacting comprises the following calculations in respect to the autoclave technology:

- Phase size distribution functions based on the integral geometry method;
- Interface boundary areas;
- Multiphase interaction energy taking into account capillary effect;
- Elastic and viscous characteristics of a deformable system based on the percolation probability model;
- System strength and permeability.

A non-linear multi-dimensional mapping based on evolutionary difference equations is used to evaluate phase mappings of unstable compositions of solidifying phases.

We examine not the vicinity of the studied non-linear phenomenon but simulate the threshold process itself based on modern postulates of non-equilibrium thermodynamics and consider the autoclave technology processes as a sequence of non-linear discrete mappings formed depending on the entropy effect.

In his papers, G.L. Brovko [9, 10] proposed to describe the structurally non-homogenous unsaturated aggregation using a complex of continuity equations, impulse equations per each phase and to use the frame reversible strain equations for the system closure.

Availability of a fine component results in system aggregation and porosity. The Kozeny-Carman equation for fine particles is not valid in this case [11]. It is noted that it's important to take into account non-linearity of the layer compressibility module and specific resistance for compressible soils as opposed to the classical soil filtration consolidation; that is why it is necessary to apply the common non-linear equation of filtration. During compression, sediment porosity permanently changes by the layer thickness. Certain authors examine particular solutions for the system obtained based on the hydrodynamic problem setting. However, not a single study takes into account irreversible phase transitions of the fine component and the process of transition of the open system into the closed one.

The efficiency of contact condensation is defined by the interaction of the binding and solid phases during the load application. The binding subsystem contains an unstable component, which transforms into a new state at certain external conditions, namely activation energy. Its interaction with the frame at the expense of efficient tensions creates local strain areas in the binder, where its properties are changed.

The analysis of different inter-particle bond mechanisms made in the paper demonstrates that the bond is based on the arrangement of the areas from the components of the subsystem with a lower hierarchy level.

Regarding the pure phase contact between particles, its possibility is defined by the area of atomic links capable to counteract hydrolysis and withstand gravity forces according to N.B. Uriev's criterion [12-14]. However, atom re-distribution is observed in the adjacent area with the increase of contact number even in this case according to the provisions of molecular dynamics.

The "complete coalescence" pattern should be recognized as applicable for the interaction of formations with the size less than critical due to higher mobility of segmented sections for liquid

particles capable to overcome the surface barrier. The probability of the lattice coincidence should be considered as small for crystals that exceed the critical size.

Decrease of inter-phase surface is accompanied by entropy decrease. The structural disorder area features gradients of chemical, temperature potential, and appearance of flows with different properties due to them.

Thus, inter-particle contacts are formed according to the polystructural hierarchic principle formulated by V.I. Solomatov: “structure in a structure”, from top downward to ion-molecular level.

Considering the solidification process as a gradual transition of interacting particles through different energy sublevels to the nearest energy well, it is necessary to state that deformation of the preliminary prepared system containing amorphous formations allows “skipping” several sublevels. At the same time, intermediate formations as various “links” accompanying these sublevels will be excluded. However, it is impossible to exclude phenomena at the ion-molecular and supramolecular levels.

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