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Challenges of Technology of Dispersed Composite Materials

This chapter considers the significant features and obstacles hindering the synthesis of one of the most widespread and widely applied among worldwide dispersed materials: cement and asphaltic concretes with a high level of structural–mechanical properties – as a demonstrative example illustrating the necessity of implementation of the approach substantiated in the Preface and in the introduction toward solution of problems of technology of dispersed systems and materials on the basis of physical chemistry of dispersed systems and physicochemical dynamics.

The further chapters also pay a great deal of attention to materials based on mineral binders and bitumens, as these materials are typical representatives of various highly filled solid phases of multicomponent dispersed composites.

By now, significant progress has been achieved in the technology of obtaining various dispersed composite materials including materials used in construction, for example, in the building of roads, bridges, and airdromes.

The increased requirements for these materials and the constructions made using them led to an increase in freight traffic density; and, accordingly, values of static, dynamic, temperature, and chemical exposure of constructions and facilities, in their turn, impose increased demands toward strength, deformation properties of dispersed composites, and their service life.

At the same time, significant importance has been attached to the increased requirements for technical and economic indices of materials in the course of operation of constructions using them.

Progress within the conventional approach to the technology of obtaining various dispersed materials, and primarily concretes, based on mineral and organic binders achieved in the recent years is related chiefly to application of cements with improved characteristics, new types of plastifiers, and modifying agents. However, transition to a qualitatively new, higher level in composite materials science under the conditions of such a conventional, and, as pointed out above, to a certain degree empirical, approach is limited by the possibilities of this conventional technology.

What are these limitations and what are the ways of overcoming them? Let us give several examples to answer these important questions.

A vivid example illustrating these limitations is the technology of obtaining cement concretes implemented at present. In particular, the design of their compositions according to the existing standards is carried out taking into account the options of the available equipment as regards the mixing, transport, casting, formation, and compaction of concrete mixtures. These parameters determine the placeability of mixtures as related to these, that is, their rheological properties (viscosity and fluidity) and, accordingly, water–cement ratio and water content.

This limitation results in a significant (in some cases, by several times) increase in the water content of concrete mixtures (up to $W/Cem = 0.4-0.5$) as compared to that required for full hydration of cement ($W/Cem \approx 0.2$) [1, 2].

At the same time, cement hydration approaching 100% during the standard 28 days of normal concrete hardening is possible only in the cases when the size of cement particles does not exceed approximately 15 μm [1, 2]. The average grain size in commercial cements is considerably higher than the stated value ($d \geq 20-25$ μm and more) [2]. Therefore, the hydration degree of standard Portland cements by the concrete age of 28 days usually does not exceed 50–60% and can reach 80% only in the case of fine quick-hardening cements. Herewith, as the time period since preparation of concrete mixes and start of interaction between cement and water until concrete placing and compaction is usually not more than 1–3 h, the hydration degree of cement during this period does not exceed several percent.

One can assume on the basis of the effect of the surface of solid phases on the properties of thin water layers [3, 4] that the thickness of these layers with changed properties does not exceed the size of 2–3 molecules of H_2O, that is, does not exceed 10 Å (1 nm). Thicker layers of 3–5 water molecules and more correspond to bulk water by their properties (viscosity, freezing point, etc.).

The amount of water covering grains of cement, sand, and chippings and characterized by its bulk properties does not exceed 1% of the given water content, that is, it is admittedly below the maximum amount required for full hydration. This means that mobility and placeability of concrete mixtures, especially during the first hours after concrete preparation, even at $W/Cem \approx 0.2$, would apparently be necessarily achieved.

However, in reality, the minimum W/Cem ratio in concrete mixtures is usually at least 0.3–0.35 even when plastifier additives are applied. And this means that excess water content determined by the requirements of placeability causes a significant increase in residual concrete porosity, decrease in its water impermeability and freezing resistance, and increase in shrinkage and creep.

Besides, it is necessary to increase cement consumption as a result of increased water content to provide the given strength of concrete. At the same time, the consequence of increased water content of mixtures predetermined by the necessity of providing the given mobility (placeability) is the further segregation of excess water, especially in the course of their transportation to the site of concrete placement and also during the first hours after placement and compaction (Figure 1.1a).
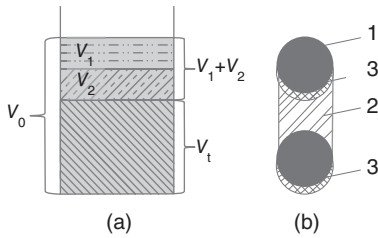
Figure 1.1 (a) Scheme characterizing water segregation in concrete mixtures: V_0 is the initial volume of the concrete mixture, V_1 is the volume of water segregated under static conditions, V_2 is the volume of water segregated in the course of transportation to the site of placement, V_t is the final volume of the concrete mixture after placement and compaction. (b) Scheme of formation of a water "lens" under coarse filler grains as a result of sedimentation: (1) grains of chippings or gravel, (2) cement solution, and (3) water "lens" under filler grains.

It is this circumstance, particularly due to sedimentation of the binder and water segregation under coarse grains (Figure 1.1b) that, to a great extent, explains reduced frost resistance and water impermeability of concretes.

However, an attempt to pass to harsh mixes with lower water content and castability without allowing for the achievement of the maximum uniformity of mixtures under mixing and formation and compaction to the required density results in the fact that the hardness of concrete calculated according to the conventional dependencies, for example, according to Equation 1.1, cannot be implemented when the critical value of given (Cem/W) is exceeded.

As seen in Figure 1.2, a drastic decrease in strength is observed above this value, though it should grow according to Equation 1.1 [5]:

$$R_{concr} = AR_{cem}(Cem/W - C) \tag{1.1}$$

where R_{concr} is the strength of concrete at the age of 28 days of normal-humidity storage; R_{cem} is the activity of cement in mPa; A is a parameter accounting for the shape of filler particles (chippings, gravel) and hardness of mixtures; C is an empirical correction of ≈ 0.5.

The following questions arise as related to the above material:

1) Why is it necessary, under actual conditions of concrete technology, to increase the water content of concrete mixtures considerably to reach the specified fluidity to the detriment of the properties of concrete and its technical–economic indicators?
2) What is the mechanism of achieving the required plasticity (placeability) and, ultimately, fluidity of concrete mixtures from the perspective of physical chemistry that results in such a considerable increase in the required amount of water?

This problem becomes even more complicated in the case of finely ground quick-setting cements, as the amount of water required for concrete mixtures based on these cements becomes even greater.
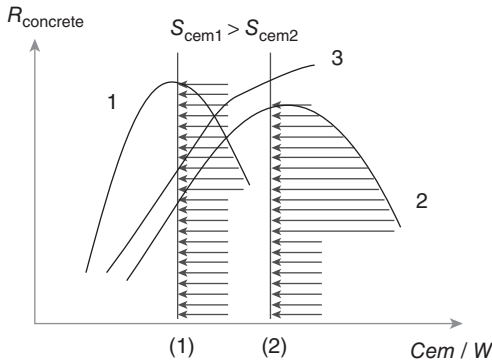
Figure 1.2 Dependence of strength of concrete on the cement/water ratio. Curves 1 and 2 correspond to concretes made on usual (2) and quick-setting, highly dispersed (1) cements (*S* is the specific surface area of cements). Curve 3 is the dependence of $R_{concrete}$ on *Cem/W* according to Equation 1.1. Arrows point to the *Cem/W* limitation relation to loss of placeability of concrete mixtures.

And, finally, the most significant issue is

3) What are the ways of resolving the contradiction between the necessity of decreasing water content in the mixtures, that is, increasing *Cem/W* and, moreover, advisability of application of finely ground (including quick-setting) and fully hydratable cements, on the one hand, and, in this connection, sharply rising viscosity, problems related to mixing, placing, and compaction of mixtures and loss of their placeability due to this cause?

Similar issues and problems arise in the technology of synthesis of other dispersed materials: of cement according to the wet method, of silicate materials, asbestos cement, concreting paper, and so on. The excessive water content in many of the above examples is due to the necessity of carrying out the processes related to fluidity (e.g., pipeline transport), deformation (particularly, in the mixing of mixture components), formation, and compaction. This excessive water is removed in many cases (particularly, by drying or vacuum treatment) in the following technological procedures. And this, in its turn, results in considerable energy losses and complication of the technological procedure. But if excessive water remains (in case of cement concretes), it causes not only formation of additional porosity but also layering (Figure 1.1a) and formation of water lenses under coarse filler grains (Figure 1.1b), which is the main cause of decreased freezing resistance, increased water permeability, shrinkage, and creep.

A lot of such examples can be provided. Whatever their diversity for implementation of technological procedures in the initial stages, that is, before the start of phase and chemical transitions accompanied by the curing of materials, the conventional technology solves a single main problem: redistribution of components in the course of the mixing, further formation, and compaction of mixtures [5], that is, occurrence of the required values of viscosity, fluidity, plasticity, and ability to change the mixture volume and shape under exposure to external forces. To

solve this problem, addition of an excess of the dispersion medium (water for many of the above materials) is in fact an induced, but the simplest, most widespread method of reducing mixture viscosity and increasing their plasticity, though often accompanied by addition of plastifiers in the conventional technology.

Let us consider another example characteristic for composites based on an organic binder, primarily, bitumen concrete.

It is commonly known that specific conditions of achieving the required plasticity−fluidity of bitumen−concrete mixtures (and mixtures of any composites based on a thermofluid binder) are determined by viscosity of bitumen, temperature parameters of mixture preparation and placing, and also bulk content, dispersion degree, and particle shape of inorganic components.

In all these cases, the so-called thermorheological effect, characterized by synergism of the temperature factor and required deformation rate during the preparation, transportation, placement, compaction, and formation of various thermoplastic mixtures, is observed.

As applied to materials based on a bitumen binder (bitumen concretes, bituminous mastics, etc.), alongside with this effect, the same as in the case of the above solutions for cement concrete, the problem of a decrease in viscosity is generally solved by addition of plasticizing agents and fluidifiers. The latter are removed by evaporation when the above materials are used after their placement.

At the same time, of considerable importance as applied to bitumen concrete is the thickness of the bituminous film on the surface of inorganic solid-phase particles [6, 7], presence and shape of additives of plasticizing agents, and possible polymer and fluidifier additives. Also, one cannot but take into account the character of interaction between the organic binder and filler surface, adhesion to it, that is, ultimately, *properties of contacts between particles at the interphase boundary* of binder−filler (aggregate).

An important element of the process of contact formation at the interphase boundary of the binder−filler is the wetting of the surface of inorganic component particles and spreading of the liquid medium over this surface [8]. This process is determined by the physicochemical properties of solid surfaces (this refers to physicochemical surface uniformity or nonuniformity), their lyophilic−lyophobic mosaic structure [9].[1]

The spreading process of non-Newtonian[2] viscous liquids, predominantly various types of binders (cement pastes, asphalt binders) and paint composites alongside the spreading of low-viscous Newtonian[2] liquids over solid surfaces plays an important role.

It should be pointed out that physicochemical literature considers mainly the processes of wetting and spreading over solid surfaces of Newtonian liquids

1) A surface that is lyophilic toward the liquid is characterized by a wetting angle lower than 90°; the wetting angle on a lyophobic surface exceeds 90° [8].
2) Newtonian liquids are liquids with viscosity that is independent of the deformation rate in a laminary flow; viscosity of non-Newtonian liquids depends on the deformation rate and decreases at its increase or even grows at an increase in the shear rate in the case of the so-called dilatant fluids [10, 11].

under static conditions [12–14]. Meanwhile, the processes of spreading of both Newtonian and non-Newtonian viscous liquids under dynamic conditions assume real significance in the technology of obtaining dispersed composites [15]. It is these conditions that are characteristic of the technology of obtaining dispersed composites.

This process, especially in high-filled systems, is preceded and (or) accompanied by procedures of component mixing, further transportation, formation, and compaction. As a rule, these operations in the technology of synthesis of dispersed materials are considered separately, individually, and independently, as sequential, and are determined by different targets and parameters of exposure of dispersed systems. At the same time, according to physicochemical concepts, these procedures are *stages of a single process of structure formation* and transition of three-phase systems (solid phase–liquid–gas; i.e., S−L−G systems) at the start of the process into two-phase ones (solid phase–liquid; i.e., S−L systems) at its end.

Such a physicochemical approach to the process of structure formation and, therefore, properties of usually multicomponent materials in the initial stages of technology of their synthesis *is the first fundamental difference* from the conventional, so-called *step-by-step* approach mentioned above.

The second important difference of the modern physicochemical approach in the technology of obtaining dispersed composites is as follows. The conventional approach provides for determination of parameters of technological operations by variation in bulk properties of multicomponent mixtures: their uniformity and viscosity (or fluidity), that is, plasticity and placeability.

Here, the most important fact usually not taken into account is that the above *bulk properties* are determined by the integral *set of interactions between individual particles*, that is, contact interactions between particles forming component mixtures at all stages of the technology of its synthesis.

In fact, formation and failure of these individual contacts in the course of the technological process form the basis for the technology of formation of the structure of composites determining their bulk properties.

The laws of formation of dispersed structures as a set of individual contact interactions between particles forming such structures are described by independent fields of physicochemical science: physical chemistry of dispersed systems and surface phenomena: *physicochemical mechanics of materials* developed by P.A. Rehbinder and his school [12, 16, 17] and, in recent years, *physicochemical dynamics of dispersed systems and materials* [18, 19].

Physicochemical mechanics, as already pointed out in the introduction, establishes the functional relationship between strength (or adhesion force) in individual contacts between solid-phase particles and bulk strength and other properties of dispersed structures and materials and also regularities of their decomposition under external exposure combined with the effect of surface-active media. At the same time, processes of formation and decomposition of dispersed structures and solids according to physicochemical mechanics are studied mainly under *static conditions*.

As already pointed out in the introduction, real diverse chemicotechnological processes of formation and decomposition of dispersed structures related to contact interactions between the dispersed phases forming them occur predominantly under dynamic conditions. These conditions, as shown in [18–20], fundamentally change the character of the relationship of contact interactions between particles and the most significant bulk (predominantly structure–rheological) properties of dispersed systems and structures forming and decomposing in such systems under *dynamic conditions*. This similarly refers to an important element of the modern technology of dispersed systems and materials: the ever wider application of surfactant plastifier additives regulating the strength and energy of interparticle contact interactions. As shown in further Chapters, the mechanism of their action under dynamic conditions differs significantly from static conditions, which must be taken into account in their choice.

All the above stipulates the necessity of considering chemical technology processes in dispersed systems and in the technology of obtaining dispersed composite materials on the basis of physicochemical dynamics.

The main problem that this new field of physicochemical science and physicochemical basics of technology of dispersed systems and materials should solve consists in establishing the fundamental regularities of *achieving the maximum fluidity* of structured dispersed systems combined with achievement of the *maximum* degree of uniformity of *dispersed structures* in high-concentration and highly dispersed systems and dispersed composite materials forming on their basis.

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Further Reading

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Schukin, E.D, Savenko, V.I., and Malkin, A.I. (2015) *Lectures on the Physical-Chemical Mechanics*, Nobel Press, Moscow, 676 pp. [in Russian]

Questions

1. Why is the specified water amount in the technology of cement concretes considerably higher than the water content required for full cement hydration?
2. What are the roles and effects of sedimentation processes related to water excess in concrete technology?
3. How does the strength of concrete depend on the dispersion degree of cement and water content? What are the limitations of mixture application in case of low water amount and high cement dispersion degree?
4. Explain the concept of contact interactions between particles and their role in the structure of dispersed composite materials.
5. What are the principal and particular characteristics of the physicochemical approach toward technology of dispersed composite materials?
6. Define physicochemical mechanics and physicochemical dynamics of dispersed systems and materials.
7. What is the role and significance of reaching the maximum fluidity of highly concentrated and highly dispersed systems in technology of dispersed composites?