Magazine of Civil Engineering

ISSN 2712-8172

journal homepage: http://engstroy.spbstu.ru/

Research article

UDC 691.32:579.66

DOI: 10.34910/MCE.118.3

Influence of biological additives on the properties of cement systems

S.V. Dudynov

National Research Mordovia State University, Saransk, Russia

✉ *dsergey@mail.ru*

Keywords: concrete, cements, mixtures, additives, microbiological synthesis, proteins, lipids, mechanical properties, hydration, environmental safety

Abstract. The object of the research is cement systems, the materials most commonly used in the construction industry. Since people interact with construction materials all the time, they should only contain harmless components; this requirement applies to modifiers as well. The existing liquefiers are obsolete; there is a need for an alternative composition and production technology. The purpose of the research is, first, to theoretically design the structure of an environmentally friendly plasticizing additive for cement systems based on fragments of natural compounds – lipids and carbohydrates. Secondly, to select a non-pathogenic microbial culture capable of synthesizing this product and the conditions for its fermentation. And finally, to study the properties of cement systems containing the synthesized biomodifier. This paper proposes novel modifiers based on fragments of natural compounds. The production process should be based on biological synthesis running through the cellular structures of microorganisms growing in a synthetic nutrient medium. A non-pathogenic microbial culture was 'tamed' to synthesize this product. The authors further designed a synthetic nutrient medium and optimized the fermentation parameters. Ten hours after the onset of fermentation, a fat-like substrate is added to the nutrient medium so that *Leuconostoc mesenteroides* would be able to synthesize the hypothesized modifier. The output is an efficient glycolipid plasticizer. X-ray diffraction analysis, a plastometer, a flow table, a cone, a viscometer, a versatile press, and an ionometer were used in this research to find the parameters of the synthesized bioadditives and cement systems based on them. The bioplasticizer injection was noted to increase the fluidity of cement mixtures by a factor of 3 to 5. The novel modifiers greatly inhibit early cement hydration when dosed at >0.8 wt.%. However, while inhibiting early structuring, these liquefiers strengthen the material in the long term (3+ months). Injecting these biological additives in the mixture at up to 0.8 wt.% produces a material that is 20÷30 % stronger than the additive-free alternative and absorbs less water while being as resistant to frost. As per our hypothesis, the microbial synthesis did in fact produce efficient cement system modifiers for industrial and residential construction that would be subject to no environmental restrictions.

Citation: Dudynov, S.V. The influence of biological additives on the properties of cement systems. Magazine of Civil Engineering. 2023. 118(2). Article no. 11803. DOI: 10.34910/MCE.118.3

1. Introduction

All of us are in constant contact with construction materials over the course of our lives. For this reason, the environmental safety of such materials is of the utmost importance.

Although the range of modern construction materials is rather vast, those where Portland cement is the binding agent occupy pride of place. Due to their abundance, they are used practically everywhere, despite the fact that they have several peculiarities and drawbacks. With regard to the aforementioned, cement systems are the object of the research.

To attenuate or decrease the defects of the latter, measures of a technological and formulation nature are used. The fact that the classic composition, which includes cement, water, sand and gravel only, has disappeared from practice for the time being confirms this point. The mandatory component of modern cement mixtures includes modifying additives, the quantity of which is rather large, and it is continuously increasing [1–10].

The additives, as a rule, possess a polyfunctional activity or some additional effect. For example, they ensure the hardening process at temperatures below zero, accelerate it, and at the same time improve mixture mobility, ameliorate the protective properties with regard to steel reinforcement, etc. However, among such a broad range, one effect dominates the rest, and based on it the compound is designated into a certain group of modifying agents.

The products possessing a plasticizing effect – diluting agents, have a special status in the whole volume of additives. Such a standing is quite natural, since a small dose of the plasticizer is accompanied by substantial changes both in the production technology of the parts, items, constructions, and in the construction and technical characteristics of the ready-made material. Moreover, they are very accessible, their cost is comparatively low, and they usually belong to the group of surface-active agents (SAA).

According to the existing gradation, there are plasticizers, superplasticizers and hyperplasticizers. And superplasticizers on the melamine and naphthaline-formaldehyde basis, possessing high technical characteristics, are widely used in construction. However, the mentioned substances are highly hazardous, which makes their use in light of the toughening environmental requirements rather dubious [11–20].

From this point of view products based on polycarboxylate or acrylic polymers, which have another molecular structure, are more preferable. The serious drawback of such compounds, however, is their high cost, low accessibility, and heightened requirements towards qualitative figures of the used cements, which inevitably creates limit at ions for their use in mass construction.

It is also worth mentioning that most efficient diluting agents are produced artificially – by means of streamlined chemical synthesis. Such a method naturally envisages the production of the target compound using special, often unique equipment, and is based on individual technology, and the chemical processes, in any case, result in often dangerous byproducts, the utilization of which is also rather expensive.

The aforementioned expressly justifies the topicality of the research of cement composites with plasticizers, since existing diluting agents have become exhausted, and must be changed both in their composition and production technology [21–33].

We believe that natural substances or materials produced using their fragments have good potential in terms of environmental figures. These are proteins, carbohydrates, lipids, nucleic acids, their derivatives and complexes. The method of producing the mentioned compounds – the source of commercial production, becomes rather important here.

In our view, the technological solution of the issue is in using biotechnology for producing the compounds with a set structure, and the subsequent (as applicable) task-oriented transformation of the produced products using the later ones as the initial raw material.

Biotechnology is based on the use of live cells – plant, animal ones, including the cells of microscopic creatures for certain purposes. In this case we suggest the fermentative cultivation of microorganisms for the synthesis and accumulation of desirable metabolites with the set composition and structure, with the subsequent use of the produced compounds as modifying agents in the cement compositions.

The microorganisms synthesize various compounds, some of which possess surface activity. Due to the large value of the surface v/s volume ratio, they are promising products capable of considerably broadening the range of additives for concretes currently used.

A live cell may be compared to a very complex system of shops, with a change of containers with organic and aqueous media, which contain various reagents. The cellular structures provide the required sequence of the successive metabolic reactions, which, if decomposed, are interrupted, and the effect begins to be produced only by hydrolytic enzymes.

The suggested concept is rather logically explained by the circumstance that a set of technological advantages is appropriate to the substances of microbial synthesis:

1. due to complete biological destruction, the products of microbial synthesis cannot contaminate the environment;
2. retain efficiency in a wide range of temperatures, pH;
3. are renewable resources;
4. have unlimited resource sources.

The use of biotechnology from the technological point of view is quite justified. We will substantiate this statement in more detail.

Alternative production processes always require huge material and financial costs to equip the factory with the necessary materials. Moreover, the installed mechanisms, engineering facilities and appliances usually cannot be used for producing other products.

By contrast, biotechnology is based on single-type processes, appliances and devices. The correct choice of the strain-producer is the main thing here. The optimization of the cultivation process is not very complex and will not take much time. Moreover, if necessary, the whole system may be reset relatively easily and quickly for the production of another target product using the same equipment and the analogous scheme, when a simple exchange of the microbial population strain and/or growing medium for its cultivation is required.

The main difficulty involves correctly determining the microorganism-producer able to generate the target compound, since this synthesis can be produced by various microscopic creatures. This compound can be constructed theoretically at the beginning, and then the required conditions for its generation must be created using the selected microbial strain.

In principle, for biosynthesis of the required product there is a theoretical possibility of using a producer from any taxonomic group: bacteria, fungi, yeast fungi, microalgae, molds, etc. The unique peculiar feature of the biotechnology must be emphasized here, which is represented as follows.

If the microbial colony does not generate the required fragment, it will be sufficient to introduce a specific reagent into the growth medium composition, thus changing the cultivation conditions in the bioreactor, forcing the producer to absorb a new substrate. The microorganisms, adapted in their development to such an unusual source of nourishment, subsequently start synthesizing it in large quantities (in such cases, the term 'accustomed to' is used).

Furthermore, the conditions required for biotechnological processes differ greatly from those under chemical effects. In particular, the main difference is that in such a case the following will not be necessary: high temperature; high pressure; catalysts, etc. Moreover, biosynthesis usually takes place at room temperature and under regular atmospheric pressure, making the production cycle much safer, easier, and making it possible to organize the production of environmentally friendly products in any climate conditions with relatively low material costs and investments.

As a rule, plasticizers are products from the surface-active agents (SAA) group.

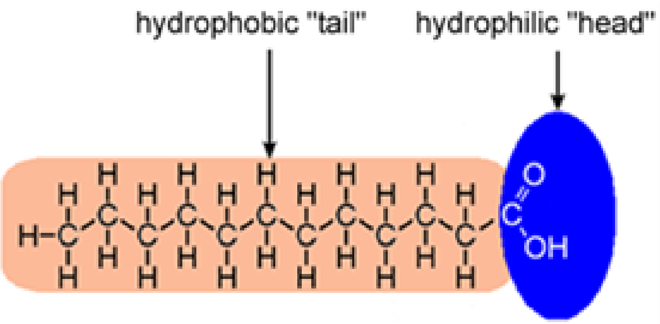

Figure 1. Structure of surface-active agents.

The structure of surface-active agents is composed of a hydrophilic constituent, represented usually by the polar group – carboxyl (—COOH), amino- (—NH_2), nitro- (—NO_2), oxi- (—OH), sulfo- (—SO_3H) and so on, and a hydrophobic hydrocarbon radical. Such a two-fold nature of SAAs gives to them special properties, in particular, the ability to adsorb at the phase boundary. Moreover, with the concentration being increased, the molecules of the surface-active agents are united into specific associates – micellae, changing their form when the critical micelle concentration (CMC) is reached.

It is known that the SAA properties are determined by the construction of diphilic components and their mutual position in the molecule. The influence of the hydrocarbon radical length and activity of functional groups are distinguished here first of all.

In our view, the compound may demonstrate plasticizing properties when the missing structural component is introduced into its composition, thereby transforming the compound into a diphilic one. That is, for the reagents having a polar group, the hydrocarbon fragment must be injected; and vice versa, the characteristic group must be added to the product containing the hydrocarbon radical. Such changes transfer any compound into the category of a surface-active agent.

As stated, the surface activity of the SAAs at other equal conditions depends on the properties of the diphilic components. Hence, we believe that the surface activity of the substance can be increased by substituting the functional groups for more active ones, increasing their number in the compound macromolecule, or by injecting additional or longer hydrocarbon radicals.

Carbohydrates account for a large share of the total number of natural compounds. Studying the structure of carbohydrates, it is easy to notice that they have an excess of hydrophilic components. However, though the mobility of the concrete mixture after the injection of carbohydrates changes, its value in this case is negative. According to our research tests, adding sugars (for example, dextrans and dextrins) to the cement mixtures decreases the mobility of the latter, with a simultaneous decrease in the strength of the hardened material.

Therefore, it is rather logical to assume that to produce an efficient sugar-based plasticizer, a hydrocarbon chain of lipids must be implanted into the latter, which may consist, for example, of a fatty acid. Injection of the hydrophobic link into the carbohydrate molecule will be accompanied by a change in the structure and molecular mass of the compound, its lyophilic-lyophobic balance, CMC, which, in turn will influence the properties of the final product, and, if the latter is injected into construction mixtures, will produce a plasticizing effect.

The synthesis of bioSAA, in our view, may take place during the development of the microbial colony only after the injection into the growing medium at a certain stage of fermentation of special ingredients – fatty acids, vegetable oil or other lipoids. This is due to the fact that, after a certain period of time, the sufficient quantity of developed cells with accumulated carbohydrates is contained in the producer population. Adding the fat-containing substrate to the growing medium composition changes the cultivation conditions, breaching the C/N ratio in favor of carbon, thus stimulating the formation of lipids [37–40].

It should be pointed out that over the course of various development stages, all types of microbial creatures must generate and accumulate carbohydrates as an auxiliary material and source of energy. Adding the reagent containing the lipid fraction (vegetable oil, oleic acid, etc.) changes the cultivation conditions, forcing the bacteria to absorb the new component. The subsequent generations of microorganisms cultivated in such conditions will be 'accustomed to' synthesizing it. The process of intensified accumulation of lipids is further enhanced by the intensive growth in the number of senescent cells, which are characterized by an increased fat content. Given the ability to maintain optimal existence conditions, the population of microorganisms tends to use the available material to construct new cells. Biochemical transformations take place simultaneously in cellular structures, accompanied by the integration of fatty acid molecules into the structure of oligomer links in the carbohydrate fragments. New glycolipid type molecules, having the following structure, are formed and accumulated during the transformation of initial substrates:

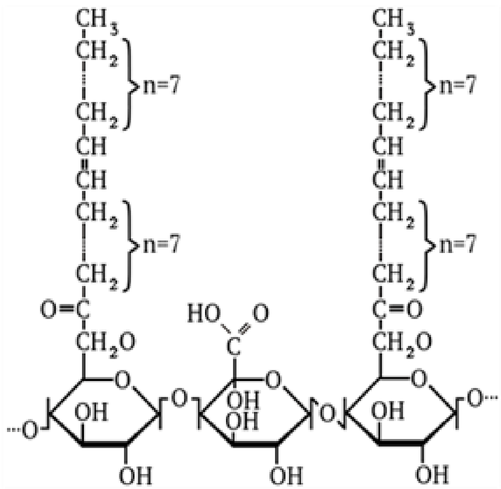

Figure 2. Structure of new glycolipid type molecules.

It is easy to notice that the structure produced is analogous to that of glycolipids. Glycolipids, as is known, possess the highest surface activity among natural SAAs [34–40].

Based on the proposed theoretical concept, we have successfully synthesized non-hazardous biomodifiers for construction mixtures.

The task of the work is to develop efficient and environmentally friendly plasticizers for construction purposes, which include or are composed of the fragments of natural compounds: 1) using the methods of biotechnology, namely streamlined microbial synthesis; 2) modification of the existing ones, without producing reagent byproducts.

To achieve the set task, the following issues must be solved:

to demonstrate the possibility of transforming the initial compounds into SAAs by means of streamlined microbiological reconstruction of their composition and structure;

to search for substances possessing the surface-active properties among natural products, i.e. those being potential plasticizers for the cement systems;

to demonstrate the expedience of using biotechnology for the synthesis of compounds with the set composition and structure;

to find strains of microorganisms suitable for cultivation in such processes;

to study the rheological properties of cement compositions with bioSAAs;

to examine the construction and technological characteristics of the cement systems with the produced biomodifiers.

2. Materials and Methods

Cement mixes were prepared using several cements, the technical performance of which is demonstrated in Tables 1 and 2.

Table 1. Cements chemistry.

Cement No.	Composition, %					
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3
1	2	3	4	5	6	7
Z1	58.7	28.31	4.21	3.44	1.41	2.3
Z2	60.27	24.55	4.50	4.05	0.82	2.64
Z3	63.46	20.58	4.74	4.23	1.74	3.21
Z4	64.9	20.8	4.2	3.5	1.1	3.0

Table 2. Cements mineralogy.

Cement No	Composition, %			
	C_3S	C_2S	C_3A	C_4AF
1	2	3	4	5
Z1	57.73	23.3	5.01	10.46
Z2	61.6	17.1	4.9	13.3
Z3	62.99	15.01	5.51	14.35
Z4	73.0	8.7	5.3	11.6

The specific surface area of the cements is 2370–2850 cm^2/g.

Samples, forms, equipment and test methods comply with EN 12350, EN 12390, CR 13901, EN 196, EN 934.

To study the structural changes in cement systems, an X-ray phase analysis was performed on the X-ray diffractometer with X-ray intensity ionization registration. Copper K_{α_1} -radiation and nickel filter were used in the study. Powder diagram was taken at room temperature in the following mode: tube current is 16 mA; voltage is 30 kV; RC time is 2 s; diagram chart speed is 720 mm/hour; recording scale range is 1000 imp/s. When determining the hydration degree (α) was in the (2Θ) 8–57º range of angles with a counter speed of 1 º/min twice with the sample repacking.

The base cement from which the cement stone of the control composition was obtained, was used as an external standard for determination of the degree of hydration of clinker minerals. In this case, α clinker of minerals is determined from the formula:

$$\alpha = \left(1 - \frac{J_\tau}{J_0}\right) \times 100\%, \quad (1)$$

where J_0 is line intensity of a given phase in the base unhydrated cement; J_τ is line intensity of the same phase in the hydrated cement.

The cement stone was formed during the hardening of the cement paste prepared with a constant water-cement ratio and a corresponding proportion of modifier additive.

By comparing the intensities of analytical lines selected for each crystal formation in time we determined the amount of unhydrated substance of cement clinker minerals.

The degree of C_4AF hydration was not determined.

To calculate the hydration of clinker minerals, the line of average intensity with d = 2.204 Å was chosen as the analytical line for C_3A; α-C_2S is the line with d = 3.869 Å; β-C_2S is the strong line with d = 2.189 Å, not overlapping the lines of other minerals; C_3S is the strongest line of intensity "100" on the 100-point scale with d = 2.776 Å.

The mobility of the concrete mix was determined by the standard cone slump. The comparison was made with the control composition.

The effect of additives on the mobility of cement mortar was made by comparing the spreads of the control composition and compositions with the additives obtained from the experiments on the shaker apparatus.

The water absorption of the material was determined by the storage of samples in water during the specified time.

The study of the structure formation process was carried out on a cone plastometer. The method consists of determining the mechanical properties of the cement mix and the nature of their change over time. Here the controlled item of the system is its plastic strength, which is calculated on the readings recorded when the cone is penetrated at the same depth. The plastic strength of the cement paste "P_m" was calculated as per the formula (2)

$$P_m = K_\alpha \times \frac{P}{h_m^2}, \text{ MPa}, \tag{2}$$

where P is load on the cone, kN; h_m^2 is cone penetration depth, cm; K_α is cone constant, moreover,

$$K_\alpha = \frac{1}{\pi} \times \cos\frac{\alpha}{2} \times \cot\frac{\alpha}{2}, \tag{3}$$

where α is cone-apex angle (in its axial plane).

During concreting, the process of material hardening can occur both under normal conditions (t = 291-–294 K, W = 95–100 %), and in curing. Bearing this in mind, the following curing mode was adopted (in hours): preliminary curing + temperature rise + isothermal warming + temperature drop = 2 + 3 + 7 + 4. The temperature of isothermal warming is 353±2 K [41–44].

Generally, bioadditive production technology includes the following operations:

- preparation of a sterile synthetic medium;
- sowing fermentation – inoculum cultivation;
- fermentation.

When choosing a producer culture for biomodifiers, not only its ability to synthesize the necessary compounds fast and in great numbers, but also their localization is of significant importance. According to this indicator, microorganisms can be divided into two groups: 1 – microorganisms that accumulate metabolic products inside the cell (intracellular); 2 – microorganisms that get them into the cultural liquid (extracellular). It stands to reason that to extract intracellular metabolites, it is necessary to destroy cellular structures someway, which naturally complicates the process at the instrument level. Therefore, in some cases, less productive cultures that produce extracellular metabolites may be preferable to highly productive ones that accumulate biosynthesis products in cellular organoids. Here, the individual peculiarities of the microbial population can be crucial in terms of the choice of a particular species [45–48].

Leuconostoc mesenteroides bacteria cultivated on a synthetic medium were selected as a producer. The basis for this decision is the following factors:

The first and most important factor is that the microbial culture is not pathogenic.

Second, biosynthesis compounds formed during the cultivation of colonies are localized not in cellular organoids, but outside them. That is, we will not require additional operations for their extraction subsequently. Consequently, the process chain becomes much shorter and simpler at the instrument level.

Third, *Leuconosloc mesenteroides* accumulates metabolic products encapsulated. Moreover, the walls of the capsule consist of structures that are easily destroyed by the exposure of even weakly alkaline media. Thus, after fermentation, additional stages for extracting the preparations will not be required, since the hydration reaction of the cement clinker is accompanied by the formation of calcium hydroxide, which gives the pore liquid pH = 7 or more, which is why the biomodifiers get into the cement system directly. Therefore, the additive can be introduced in the form of a cultural liquid at a particular.

Fourth, the use of a synthetic (artificial), rather than a natural medium for the growth of the microbial population ensures the stability of the properties of the synthesized product.

We used the following composition of the medium: potassium chloride is 0.1 g; magnesium sulfate is 0.1 g; potassium phosphate monobasic is 1.0 g; disodium hydrogen phosphate is 2.5 g; ammonium chloride is 0.5 g; Mohr's salt is 0.01 g; paraaminobenzoic acid is 0.05 g; peptone is 0.2 g; refined sugar is 100 g; apyrogenic water (water for injection) is 1000 ml; oleic acid – 0.14 g (for the synthesis of the product with the index “O-1”); – 0.18 g (for the synthesis of the product with the index “O-2”). A sterilization stage is required to prevent the development of other microbial organisms, including wild ones. Sterilization was carried out in one of the temperature conditions: 378 K – 20 minutes or 390 K – 10 minutes.

To get glycolipid plasticizers, the bacterial culture was grown in flasks with a medium in a shaking mode (160 rpm). The culture medium was inoculated as 1 tube with seed per 100 ml of medium. Ten hours after the start of cultivation, a specific substrate (vegetable oil or oleic acid) was added to the medium.

The duration of the cultivation period was 24–48 hours at a temperature of 296–298 K. Considering the fact that the number of accumulating lipids in the individual cells of the producer colony increases with aging, the preference should be given to processes with a longer duration. After completion of the fermentation, the surfactant of the microbial synthesis of the glycolipid base is ready for use as an additive in cement systems. If the components containing a fat-like substrate (vegetable oil, oleic acid, etc.) are excluded from the composition of the medium, the selected bacterial strain that is not “accustomed” to the synthesis of the lipid fraction accumulates only polysaccharides, and the biomodifier is not formed.

During the experiments on the selection of parameters for fermentation, the following factors significantly influence on the indicators of the resulted substances:

- the oxygen concentration and carbon dioxide in the cultural liquid;
- stimulating additives;
- time of specific substrate introduction;
- cultivation duration;
- mixer rotation speed.

Moreover, when introducing the type and dosage of the added reagent have a significant impact on the quality indicators of the synthesized biomodifier.

3. Results and Discussion

Without insight into metabolic reactions occurring in the course of fermentation, we should note that chemically the resulting compounds are typical surfactants.

Therefore, the operating principle of the resultant biomodifiers can be briefly described as follows.

By adsorbing on cement system’s components with a polar «head» and an outward-orientated «tail», surfactant molecules smoothen sharp edges, angles, and surface roughness, thereby making grains more rounded, which in turn makes the mix more flowing. In addition to the above, we should note that with the hydrocarbon «tails» being orientated outwards the hydrophobic repulsive forces occur between them that hinder the grain aggregation process. I.e., synergism effect is obvious here that intensifies the plasticizing effect.

But an adsorbed surfactant layer has also another effect.

Hydrocarbon chain “pale fencing” intrinsically hinders water molecules’ penetration to the surface of clinker grains, which extends the time of setting and solidifying. This fact is supported by hydration process deceleration, which is clearly seen when comparing charts that demonstrate plastic strength changing of the reference (plain) cement system and mixes with a biomodifier.

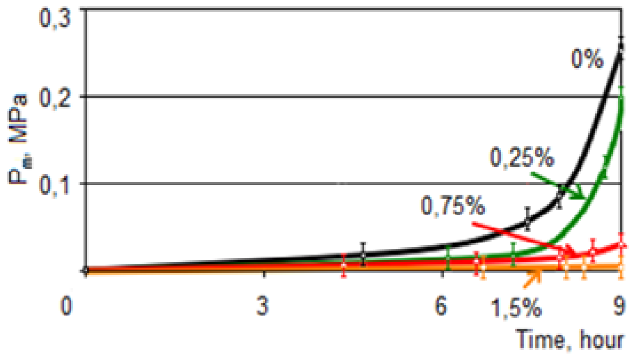

Figure 3. Structure formation of a cement paste with a glycolipid additive (% of cement).

In terms of plasticizing effect comparison, it should be highlighted that this effect is determined by a quantitative dosage of the fluxing agent added and is not influenced by a qualitative composition – paste, mortar, or concrete mix. That means that developed modifiers increase the flowability of cement pastes, cement mortars, and concrete mixes. The same plasticizing technique from the proposed bioadditives emerges in systems prepared using the different cements, though their quantitative characteristics vary widely.

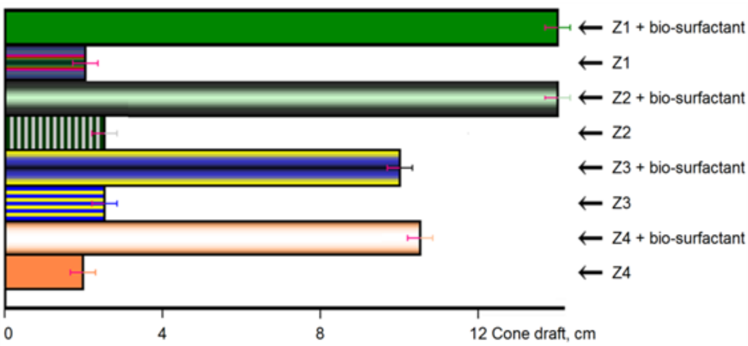

Figure 4. Bioflux effect on the flowability of systems prepared using the different cements.

In general, though, greater importance of fluxing is characteristic of poly-cement mixes.

In-process devices and designs are often exposed to negative environmental factors, specifically – to sub-zero temperatures. Moreover, the concrete freeze-thaw resistance is significantly impacted by the number of open water penetrable pores. The biosurfactant use in certain dosage appeared to not compromise the freeze-thaw resistance. This parameter of a modified concrete in the dosage of 0.2~0.3 % of cement mass retains the level of a plain composition, as demonstrated by sample compression test results after multiple freeze-thaw cycles (see Fig. 5).

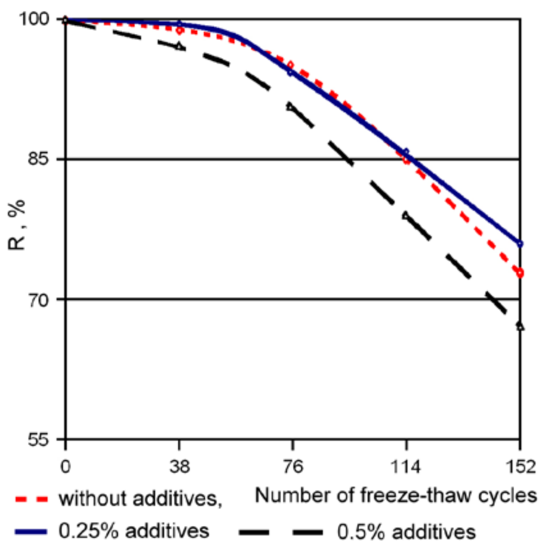

Figure 5. Material strength change with exposure to various biomodifier dosages after alternating freezing and thawing.

When exposed to sub-zero temperatures, the structure of a construction materials undergoes negative changes. Ultimately, developing destructive processes cause material breakage regardless of the initial mechanical strength value. With that in mind, one of the most significant features of concrete is its porosity [49–51]. In addition, we can have a certain understanding of a pore space within the structure of hardened concrete via its water absorption kinetics. The nature of charts shows that the use of an additive does not result in a drastic concrete porosity change.

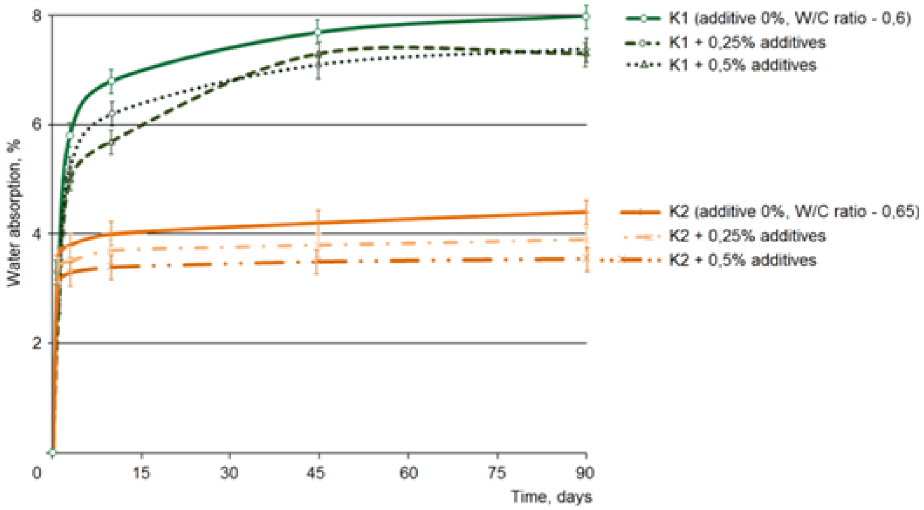

Figure 6. Concrete water absorption kinetics versus different bioadditives' dosages.

Lines showing the mass increase of samples formed of concrete mixes with various glycolipid modifier dosage and reference (plain) composition are strictly synchronous. It proves that the pore size has not changed. However, general porosity of a material with added fluxing agent is lower than in a concrete made of similar blank mix compositions, which is evidenced by a higher position of the reference composition line.

There are rather interesting results with changes in strength characteristics of a material with various content of biomodifier hardening in normal conditions.

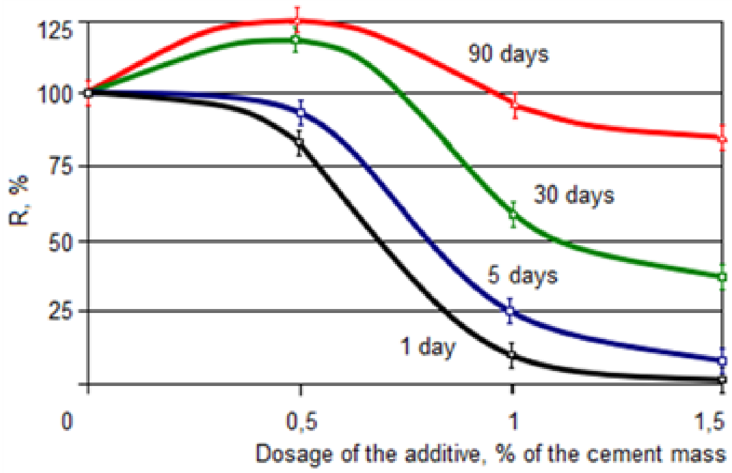

Figure 7. Time variation of the strength of a cement mortar with a glycolipid additive under normal hardening condition.

Apparently, short-term strength of blocks formed of mixes with an additive is more than 0.8 % lower than corresponding values of a reference lot (plain). However, this difference gradually fades away over time and with the lapse of three months the strength characteristics of samples made of the blank mix no longer exceed those of compositions with a plasticizer.

The findings are a solid proof of screening effect of the adsorbed biosurfactant layer on the surface of cement grains.

On the basis of these findings, we can conclude that it is quite possible to add glycolipid bioadditive of up to 0.8 % of cement mass. Such dosages make the modified material strength not only comparable to similar parameters of a reference composition, but even higher by up to 25 % at three months.

The cement clinker minerals hydration in mixes containing a glycolipid modifier after hygrothermal processing may be evaluated by the resulting X-ray phase analysis of diffraction patterns shown on.

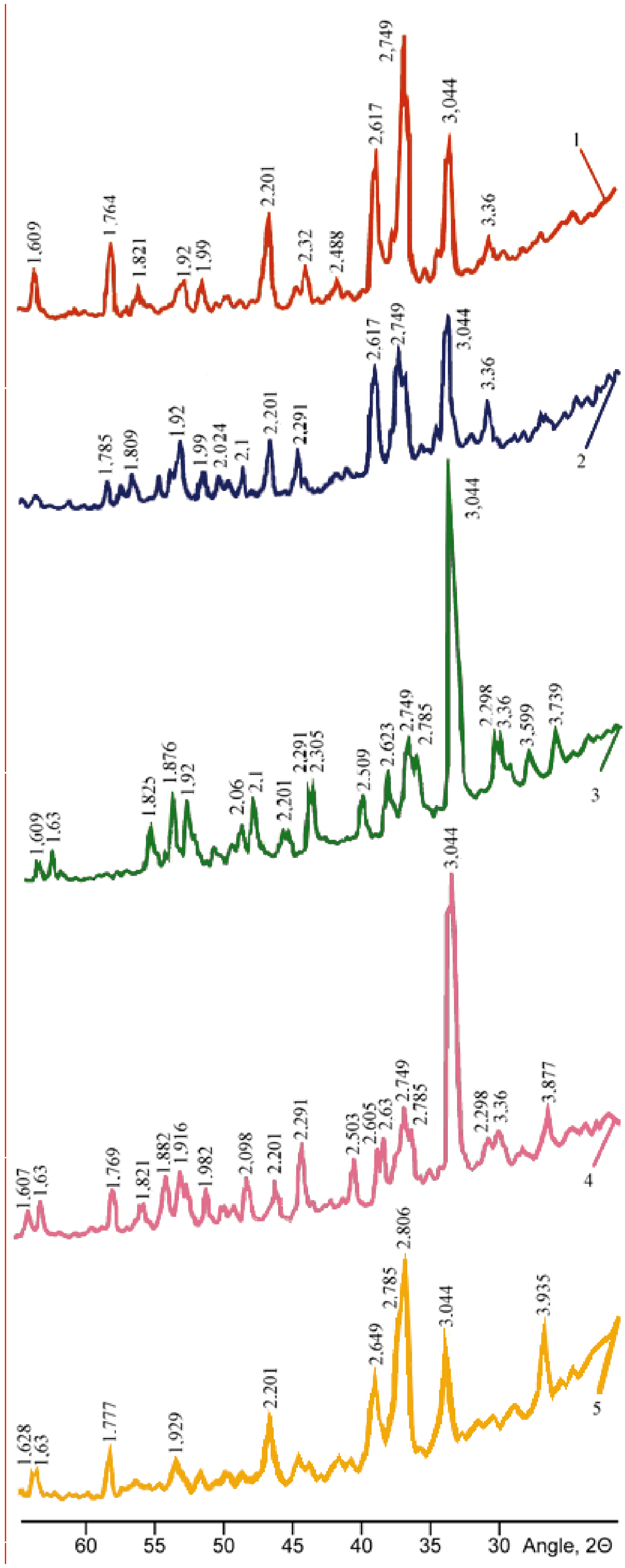

Figure 8. X-rays of a cement stone with a glycolipid plasticizer after hygrothermal processing. Additivecontent (% ofcement): 1 – 0; 2 – 0.1; 3 – 0.25; 4 – 0.5; 5 – 1.

The glycolipid additive compositions show the lower degree of hydration of base minerals than in a reference (plain) composition mix with a higher crystalline hydrate content than in any other mixes.

Thus, the use of biosurfactants hinders the hydration of clinker minerals during hygrothermal processing of a material, with the perfectly structured compounds to form. The latter is confirmed by predominance of single peaks on powder diffraction patterns of compositions with an additive compared to fuzzy apexes on the reference composition X-ray.

Occurring changes may be the result of additive sorbing on hydration products and hindering structure forming processes. Hydration inhibition by an adsorption layer of a modifier has the most significant impact on the material strength at early stages of hardening. During this period there are significantly less hydrated newgrowths formed in mixes with a bioflux, which means their strength characteristics are lower. In the course of time the negative impact of an additive (on strength characteristics) weakens. It is quite possibly related to activation of hydration products' surfaces by modifier's molecules followed by embedding of these molecules into the forming material structure.

Structure forming inhibition will inevitably affect the cement system flowability as well. Cement agent hydration deceleration along with newgrowths forming processes leads to release of a portion of water, which is an additional factor for plasticizing effect increase. These are the conditions that are created by introduction of glycolipid modifiers into the composition of cement mixes.

One may evaluate the extent of impact of a fluxing agent dosage on the flowability of a mortar mix by the charts shown on Fig. 9.

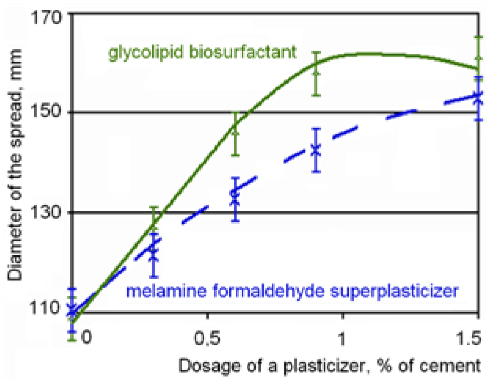

Figure 9. Impact of a modifier on the mortar spread (cement – Z1, mortar:sand = 1:3, W/C = 0.64).

As we can see, the most significant increase in flowability is observed at the consumption rate of a plasticizer of up to 1.5 % of cement mass, while its higher amount is not so effective. In fact, a higher additive dosage is not reasonable, as fluxion is disproportionate to its consumption rate. We believe that these observations are related to saturation of surfaces of cement paste newgrowths at agent introduction of no more than 1.5 % of cement mass. Further concentration of plasticizer molecules in a dispersion medium doesn't lead to its fluxion increase, but only hinders the formation of new phase contacts instead, which inhibits the new structure forming [52–55].

This fact is especially obvious on the charts of cement paste setting in the presence of bioadditives.

Therefore, molecules of the fluxing agent in a dispersion system are adsorbed on surfaces of highly-dispersive components by polar groups, creating a molecular layer with outward-orientated hydrocarbon radicals. Due to worsening of hydration conditions the structure forming processes are decelerated, and strength development shifts to the long run.

Notably, the most significant effect of biomodifier's adsorption layers is observed in mixes with highly-dispersive grains and anisometric particles with sharp edges, angles, and defective surfaces. In this case the grain shape is changed due to smoothening of sharp edges, angles, and surface irregularities by adsorbed layers of biosurfactant molecules that simultaneously create a structural-mechanical barrier. Cement paste, the most active concrete mix component, is such a system. That is why, additive's molecules adsorbed on surfaces of concrete mix disperse components draw them aside, acting as a kind of lubricant as well. In turn, highly-dispersive grains covered with an adsorption surfactant layer along with particles that have anisometric shape hinder aggregation of larger components, thereby enhancing cement system fluxing.

This is a general, basic, and brief description of the essence of processes that take place in cement systems with added biomodifiers.

The existing liquefiers are obsolete; there is a need for an alternative composition and an alternative production technology.

Alternative modifiers should be found among natural compounds or synthesized from their fragments; industrial production of such modifiers should use biotechnology.

The authors theorized upon a cement plasticizer based on fragments of natural compounds, lipids and carbohydrates, and theoretically constructed its structure.

They picked a non-pathogenic microbial culture, *Leuconosloc mesenteroides*, and 'tamed' it to synthesize this product.

The authors further designed a synthetic nutrient medium and optimized the fermentation parameters.

Experiments showed that adding the newly made biological surfactants to the cement composition delayed the structuring. Higher doses (>0.8 wt.%) resulted in the most prominent delay in the early hydration of crystalline cement formations. The additives would be adsorbed on the finely dispersed components of the binder, thus preventing the water-clinker interface.

Cement systems with these biomodifiers showcased absorption combined with chemical effects, i.e. chemisorption. Chemisorption was the first of all of the characteristics of the components in the surficial active centers. As a result, the most active components were neutralized early in hydration.

Thus, the microbially synthesized surfactant had a strong liquefying effect on cement systems of any composition regardless of the binder concentration.

The authors found that a high dosage (>0.8 wt.%) is strongly not recommended for glycolipid liquefiers. The reason is that it not only inhibits clinker hydration but also reduces the strength of the cured concrete.

On the other hand, while early structuring may be slower, such biomodifiers do strengthen the cured material in the long term. Experiments showed that the optimal dosage of the liquefier (up to 0.8 % wt.%) produced a material that was 20÷30 % stronger than its additive-free counterpart. Frost resistance was not compromised. In addition, cement composites with the glycolipid additive were noted to absorb less water.

Based on the theoretical concept put forward, the authors successfully synthesized friendly biomodifiers for construction mixes.

Thus, microbial synthesis produced efficient cement system modifiers that would be subject to no environmental restrictions for industrial and residential construction.

References

1. Gambhir, M.L. Concrete Technology: Theory And Practice. 5th Edition. McGraw Hill Education (India). New Delhi, 2013. 792 p.
2. Kalashnikov, V.I., Tarakanov, O.V., Kusnetsov, Y.S., Volodin, V.M., Belyakova, E.A. Next generation concreteon the basis of fine-grained dry powder mixes. Magazine of Civil Engineering. 2012. 34(8). Pp. 47-53. (rus). DOI: 10.5862/MCE.34.7.
3. Nagrockienė, D., Girskas, G., Skripkiūnas, G. Properties of concrete modified with mineral additives. Construction and Building Materials. 2017. 135. Pp. 37–42. DOI: 10.1016/j.conbuildmat.2016.12.215
4. Vu, Q.H., Pham, G., Chonier, A., Brouard, E. et al. Impact of different climates on the resistance of concrete to natural carbonation. Construction and Building Materials. 2019. 216. Pp. 450–467. DOI: 10.1016/j.conbuildmat.2019.04.263
5. Guadalupe Sierra-Beltran, M., Jonkers, H.M., Schlangen, E. Characterization of sustainable bio-based mortar for concrete repair. Construction and Building Materials. 2014. 67 (C). Pp. 344–352. https://doi.org/10.1016/j.conbuildmat.2014.01.012
6. Ikumapayi, C.M., Adeniji, A.A., Obisesan, A.A. et al. Effects of Carbonation on the Properties of Concrete. Scientific Review. 2019. 5(12). Pp. 205–214.
7. Yoshihiko Ohama. Additives to concrete and mortars. WilliamAndrew. 1995. 246 p.
8. Li, Q., He, Ch., Zhou, H. et al. Effects of polycarboxylate superplasticizer-modified graphene oxide on hydration characteristics and mechanical behavior of cement. Construction and Building Materials. 2021. 272(22). DOI: 10.1016/j.conbuildmat.2020.121904
9. Casagrande, C.A., Jochem, L.F., Ongherob, L. et al. Effect of partial substitution of superplasticizer by silanes in Portland cement pastes. Journal of Building Engineering. 2020. 29. DOI: 10.1016/j.jobe.2020.101226
10. Stark, J. Recent advances in the field of cement hydration and microstructure analysis. Cement and Concrete Research. 2011. 41(7). Pp. 666–678. DOI: 10.1016/j.cemconres.2011.03.028
11. Bungey, J.H., Grantham, M.G. Testing of Concrete in Structures. Taylor and Francis. 4th edition.CRC Press. London, 2014. 352 p.
12. Morin, V., Tenoudji, F., Cohen, A., Feylessouli et al. Superplasticizer effects on setting and structuration mechanisms of ultra-high-performance concrete. Cement and Concrete Research. 2001. 31. Pp. 63–71.
13. Han, S., Van, P.Y., Kong, X.M. Study on the compatibility of cement-superplasticizer system based on the amount of free solution. Technological Sciences. 2011. 54 (1). Pp. 183–189. DOI: 10.1007/s11431-010-4174-2
14. Wang, K., Jansen, D.C., Shah, S.P. et al. Permeability study of cracked concrete. Cement and Concrete Research. 1997. 27(3). Pp. 381–393.

15. Rubio-Hernández, F.J., Adarve-Castroa, A., Velázquez-Navarrob, J.F. et al. Influence of water/cement ratio, and type and concentration of chemical additives on the static and dynamic yield stresses of Portland cement paste. Construction and Building Materials. 2020. 235. 117744. DOI: 10.1016/j.conbuildmat.2019.117744
16. Khaemba, D.N., Azam, A., See, T.-L., Neville, A. et al. Early strength development in concrete using preformed CSH nano crystals. Tribology International. 2020. 146. 106243. DOI: 10.1016/j.triboint.2020.106243
17. Kiski, S.S., Ageyev, I.V., Ponomarev, A.N., Kozeyev, A.A., Yudovich, M.Ye. Investigation of carboxylate plasticizer modification potential in modified fine-grained concrete mixes. Magazine of Civil Engineering. 2012. 34(8). Pp. 42–46. (rus). DOI: 10.5862/MCE.34.6.
18. Sakai, E., Kakinuma, Y., Yamamoto, K., Daimon, M. Relation between the Shape of Silica Fume and the Fluidity of Cement Paste at Low Water to Powder Ratio. Journal of Advanced Concrete Technology.2009. 7(I). Pp. 13–20. DOI: 10.3151/jact.7.13
19. Choi, Y.W., Kim, Y.J., Shin, H.C., Moon, H.Y. An Experimental Research on the Fluidity and Mechanical Properties of High-Strength Lightweight Self-Compacting Concrete. Cement and Concrete Research. 2006. 9. Pp. 1595–1602. DOI: 10.1016/j.cemconres.2004.11.003
20. Azam, A., Dorgham, A., Khaemba, D.N., Salehi, F.M. Understanding the role of surface textures in improving the performance of boundary additives, part II: Numerical simulations. Tribology International. 2020. 152:106252. DOI: 10.1016/j.triboint.2020.106252
21. Weichert, D., Ponter, A. (Eds.). Limit States of Materials and Structures: Direct Methods. Springer Netherlands. 2009. 320 p.
22. Young, J.F. A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures. Cement and Concrete Research. 1972. 2(4). Pp. 415–433.
23. Chaudhari, O.A., Biernacki, J., Northrup, S.H. The Effect of Select Organic Compounds on Hydration of Portland Cement: Molecular Scale Insights. Annual Conference: American Ceramic Society. Cement Division. 2016. Evanston, Illinois.
24. Das, S., Ray, S., Sarkar, S. Early strength development in concrete using preformed CSH nanocrystals. Construction and Building Materials. 2020. 233. 117214. DOI: 10.1016/j.conbuildmat.2019.117214
25. Okamura, H., Ozawa, K., Ouchi, M. Self-compacting concrete. 2000. 1 (1). Pp. 3–17. DOI: 10.1680/STCO.2000.1.1.3
26. Wiktor, V., Jonkers, H.M. Quantification of crack-healing in novel bacteria-based self-healing concrete. Cement and Concrete Composites. 2011. 33 (7). Pp. 763–770. DOI: 10.1016/j.cemconcomp.2011.03.012
27. Maruya, E., Osaki, M., Igarashi, H. Relationships between Rheological Constant of Cement Paste and Fluidity of High-Fluidity Concrete. Journal of Advanced Concrete Technology. 2006. 4 (2). Pp. 251–257. DOI: 10.3151/jact.4.251
28. Han, B., Zhang, L., Ou, J. Self-Compacting Concrete. In: Smart and Multifunctional Concrete Toward Sustainable Infrastructures. 2017. Pp. 11–36.
29. Wingender J., Neu T.R., Flemming H.C. What are bacterial extracellular polymeric substances? Microbial Extracellular Polymeric Substances. Springer. Berlin Heidelberg. 1999. Pp. 1–19.
30. Sierra-Beltran, L., Jonkers, H.M. Crack self-healing technology based on bacteria. Journal of Ceramic Processing Research. 2015. 16(S1). Pp. 33–39.
31. Tziviloglou, E., Tittelboom, K.V., Palin, D., Wang, J. Bio-Based Self-Healing Concrete: From Research to Field Application. Advances in Polymer Science. 2016. Pp. 345–385. DOI: 10.1007/12_2015_332
32. Jonkers, H.M. Self-healing concrete: a biological approach. In: van der Zwaag S. (Ed.). Self-Healing Materials: An Alternative Approach to 20 Centuries of Materials. Springer Science. 2007. Dordrecht. Pp. 195–204.
33. Jonkers, H.M., Thijssen, A., Muyzer, G., Copuroglu, O. et al. Application of bacteria as self-healing agent for the development of sustainable concrete. Ecological Engineering. 2010. 36(2). Pp. 230–235. DOI: 10.1016/j.ecoleng.2008.12.036
34. Lim, J.L.G., Ramanb, S.N., Lai, F.-Ch., Mohdet, M.F. al. Synthesis of nano cementitious additives from agricultural wastes for the production of sustainable concrete. Journal of Cleaner Production. 2018. 171. Pp. 1150–1160. DOI: 10.1016/j.jclepro.2017.09.143
35. Christofi, N., Ivshina, I. Microbial Surfactants and Their Use in Soil Remediation. In: Bioremediation of Aquatic and Terrestrial Ecosystems. 2005. Pp. 311–327. DOI: 10.1201/b11002-10
36. Gunther IV, N.W., Nuñez, A., Fett, W., Solaiman, D.K.Y. Production of Rhamnolipids by Pseudomonas chlororaphis, a Nonpathogenic Bacterium. Applied and Environmental Microbiology. 2005. 71 (5). Pp. 2288–2293. DOI: 10.1128/aem.71.5.2288-2293.2005
37. Lima, T.M.S., Procopio, Ch., Brandão, F.D., de Carvalho, A.M.X. et al. Biodegradability of bacterial surfactants. Biodegradation. 2011. 22(3). Pp. 585–592. DOI: 10.1007/s10532-010-9431-3
38. Jiang, T., Gao, Ch., Ma, C., Xu, P. Microbial lactate utilization: enzymes, pathogenesis, and regulation. Trends in Microbiology. 2014. 22 (10). Pp. 589–599. DOI: 10.1016/j.tim.2014.05.008
39. John, R.P., Nampoothiri, K.M., Pandey, A. Fermentative production of lactic acid from biomass: an overview on process developments and future perspectives. Applied Microbiology and Biotechnology. 2007. 74(3). Pp. 524–534. DOI: 10.1007/s00253-006-0779-6
40. Fakas, S. Lipid biosynthesis in yeasts: A comparison of the lipid biosynthetic pathway between the model non-oleaginous yeast Saccharomyces cerevisiae and the model oleaginous yeast Yarrowia lipolytica. Engineering in Life Sciences. 2017. 17. Pp. 292–302. DOI: 10.1002/elsc.201600040
41. Chi, J.M., Huang, R., Yang, C.C. Effects of carbonation on mechanical properties and durability of concrete using accelerated testing method. Journal of Marine Science and Technology. 2002. 10 (1). Pp. 14–20.
42. Edvardsen, C. Water Permeability and Autogenous Healing of Cracks in Concrete. Aci Materials Journal. 1999. 96(4). Pp. 448–454. DOI: 10.14359/645
43. Plank, J., Hirsch, Ch. Impact of zeta potential of early cement hydration phaseson superplasticizer adsorption. Cement and Concrete Research. 2007. 37 (4). Pp. 537–542. DOI: 10.1016/j.cemconres.2007.01.007
44. Mander, J., Adams, L.D., Larkin, E.E. A Method for the Determination of Some Minor Compounds in Portland Cement and Clinker by X-Ray Diffraction. Cement and Concrete Research. 1974. 4. Pp. 533–544.
45. Groot, W.J., Borén, T. Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand. The International Journal of Life Cycle Assessment. 2010. 15(9). Pp. 970–984. DOI: 10.1007/s11367-010-0225-y
46. Bazan, N.G. (Eds.). Function and Biosynthesis of Lipids. Springer. 2012. 646 p.

47. Van Hamme, J.D., Ward, O.P. Physical and Metabolic Interactions of Pseudomonas sp. Strain JA5-B45 and Rhodococcus sp. Strain F9-D79 during Growth on Crude Oil and Effect of a Chemical Surfactant on Them. Applied and Environmental Microbiology. 2001. 67(10). Pp. 4874–4879. DOI: 10.1128/AEM.67.10.4874-4879.2001

48. Mors, R.M., Jonkers, H.M. Feasibility of lactate derivative based agent as additive for concrete for regain of crack water tightness by bacterial metabolism. Industrial Crops and Products. 2017. 106. Pp. 97–104. DOI: 10.1016/j.indcrop.2016.10.037

49. Fantilli, A.P., Kwon, S., Mihashi, H., Nishiwaki, T. Synergy assessment in hybrid Ultra-High Performance Fiber-Reinforced Concrete (UHP-FRC). Cement and Concrete Composites. 2018. 86. Pp. 19–29. DOI: 10.1016/j.cemconcomp.2017.10.012

50. Fernández, Á., García Calvo, J.L., Alonso, M.C. Ordinary Portland Cement composition for the optimization of the synergies of supplementary cementitious materials of ternary binders in hydration processes. Cement and Concrete Composites. 2018. 89. Pp. 238–250. DOI: 10.1016/j.cemconcomp.2017.12.016

51. Nguyen, H., Adesanya, E., Ohenoja, K., Kriskova, L. et al. Byproduct-based ettringite binder – A synergy between ladle slag and gypsum. Construction and Building Materials. 2019. 197. Pp. 143–151. DOI: 10.1016/j.conbuildmat.2018.11.165

52. Flatt, R., Schober, I. Superplasticizers and the rheology of concrete. Understanding the Rheology of Concrete. Woodhead Publishing Series in Civil and Structural Engineering. 2012. Pp. 144–208. DOI: 10.1533/9780857095282.2.144

53. Bauchkar, S.D., Chore, H.S. Effect of PCE superplasticizers on rheological and strength properties of high strength self-consolidating concrete. Advances in Concrete Construction. 2018. 6 (6). Pp. 561–583. DOI: 10.12989/acc.2018.6.6.561

54. Superplasticizers and Other Chemical Admixtures in Concrete. Proceedings Eleventh International Conference. Editors: V. Mohan Malhotra, Pawan R. Gupta, Terence C. Holland. Ottawa. ON. 2015. 513 p.

55. Plank, J., Ilg, M. The Role of Chemical Admixtures in the Formulation of Modern Advanced Concrete. 3rd International Conference on the Application of Superabsorbent Polymers (SAP) and Other New. 2019. 24. Pp. 143–157.

Information about author:

Sergey Dudynov*, Doctor of Technical Science*
ORCID: https://orcid.org/0000-0002-0934-549X
E-mail: dsergey@mail.ru

Received 28.10.2020. Approved after reviewing 28.09.2022. Accepted 30.09.2022.