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COLLAGEN AGENT TECHNOLOGY FOR FOAM CONCRETE PRODUCTION

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ABSTRACT

We have developed protein foam agent on the basis of collagen raw material. Collagen should destructed in soft mode at $Ca(OH)_2$ content of 2.0-2.5% and temperature of not higher than 120…125°C. Such hydrolysis mode provides complete retention of amino acids and break of disulfide groups (–SH), which leads to intensive protein foaming. The highest foaming ability of the considered agent is achieved at pH 5.80…5.87. Foam stability increases up to several hours as a consequence of addition of non-ionogenic or ampholytic high molecular surfactants to main foam agent. Additives of this family create strongly structured adsorption layers and films which retain high bulk of liquid in film. We propose the use of polyoxyethylene with molecular weight of higher than 1 million and carboxymethyl cellulose (CMC) with substitution degree higher than 0.8 and polymerization degree higher than 500 as such stabilizing additives. Duration of curing upon production of foam concrete on the basis of protein foam agent can be reduced by addition of calcium nitrite-nitrate. Addition of these salts reduced cement curing duration by 35-65 min, as well as increased foam stability, which can be attributed to additional swelling of protein as a consequence of weakening of intermolecular bonds in the protein structure. Site of connection of salt cations to protein are primarily lateral amino and carboxyl as well as hydroxyl groups.

Keywords: collagen raw material, hydrolysis, hydrolysis mode, foam agent, physiochemical properties, foam concrete mixture, foam concrete.

INTRODUCTION

The issue of energy saving in construction industry, highlighted in Specifications SNiP RK 2.04-03-2002, Construction heat engineering, defined intensive development and production of efficient inexpensive materials with superior thermal and physical properties.

The rates of urban development are high nowadays; it is required to increase production of foam concrete products. At present scientific and engineering backgrounds of production of aerated concrete products are developed, in particular - non-autoclaved foam concretes, which meet the requirements of energy saving.

Indian researchers analyzed compatibility of foam agent with chemical additives in foam concrete. Herewith, coarse filler and reinforcement were used in the composition of foam concrete, including light fibers. In addition, operation lifetime of foam concrete and influence of various factors on the properties of foam concrete were studied (Ramamurthy, *et al*. 2009).

Foam concrete on the basis of three mixes and their structure in cured state were studied: compression strength of 0.74 MPa and heat conductance of 0.054 W/m (Jiang, *et al*., n.d.).

It was established elsewhere (Mugahed Amran, *et al*., n. d.) that the use of foam concrete decreases foundation load, promotes energy saving, as well as reduces costs of construction. In addition, the use of foam concrete reduces estimated costs for transportation in comparison with concrete.

Recommendations by Korotyshevskii, formulated upon development of energy saving technology of high efficient foam concretes, can be considered as criticism of the work (Shintemirov, *et al*. 2016). He states unambiguously that preparation of foam concretes by dry foam mineralization is possible only with low-expansion foams (Korotyshevskii 1999). That work describes original technology of foam concrete with fine porosity (pore diameter less than 0.8 mm) using turbulent cavitation mixer.

At first glance this technology should be implemented commercially on wide scale, as pretends Korotyshevskii (Korotyshevskii 1999). However, more detailed study of this technology revealed some drawbacks, in particular -- application of complicated mixers and metering devices. Generation of pores in concrete mix when all its components including foam agent are loaded into the mixer hinders the process control. Foam concretes obtained by means of this technology are not characterized by steady properties, since the pressurized foam, when it leaves reactor, expands drastically and the structure of foam concrete becomes coarse porous. In addition, foam concrete obtained by means of this technology cannot be always reproduced in terms of structural properties. Thus, while implementing the technology of foam concrete we declined this barotechnology.

Currently the following conclusions can be made on the basis of this overview of scientific publications and with consideration for practical experience:

a) foam concrete is an efficient heat insulating and structural material;

b) local raw material can be used for production of high quality foam concrete;

c) foam concrete quality depends on technology of its production, type of applied foam agent, activity of binder, dispersity of silica component and type of concrete modifying agents.

Physical and engineering properties of foam concretes can be significantly improved not only by means of chemical additives but also by activation of cement and sand. Practical implementation of this approach with the aim of obtaining of required properties is described elsewhere (Solov'ev, 1990; Abaldova and Karpeev, 1980; Podsoblyaeva, 1981).

Thus, Chernykh, Mashtakov, and Shchibrya proved positive influence of chemical additives on quality improvement of heat insulating foam concrete. They proposed complex chemical additives which facilitate immediate demoulding of items and elimination of steam curing (Chernykh, *et al*. 1998; Chernykh, *et al*. 1999). Unfortunately, these researchers focused their attention on synthetic foam agents on the basis of sodium alkyl sulfates which are inferior to foreign products in terms of foam stability, for instance, Neopor System foam agent. In addition, these works do not provide data on compositions of the applied chemical compositions and mechanisms of their action.

The experience by Ukhova (Ukhova and Usova 1983) should be mentioned, who developed compositions of complex additives containing caustic soda and carboxymethyl cellulose, thus providing conditions for normal structure formation of aerated concrete mix. However, application of carboxymethyl cellulose leads to increase in times of initiation and completion of cement curing, and in combination with caustic soda increases porosity of cement stone. Operation lifetime of such concretes is not high. In addition, our experiments demonstrated that upon increase in pH of foam agent solution in excess of 8, foaming ability of protein agent, for instance, keratin agent, sharply drops. This fact is peculiar for all protein surfactants, since the highest foam yield is achieved at pH value close to protein isoelectric point (Shintemirov, *et al*. 2007). Under such conditions it is impossible to obtain foam concrete of required properties and quality (Shintemirov and A. Ismail, 1989). Thus, we decided not to apply caustic soda for acceleration of curing of non-autoclaved foam concrete.
Experience of application of waterproofing agents for production of foam concrete should be mentioned.

Techniques of decrease in water absorption using their surface and bulk water proofing are described elsewhere e (Gorlov, 1989; Rozenfel`d and Vasil`eva, 1974; Baranov, *et al*. 1974).

We believe that surface water proofing cannot be considered as an efficient method of improvement of thermal and physical properties of foam concrete, which agrees with the data by Moskvin *et al*.

Surface hydrophobization of building materials and products does not provide long term reliable operation of structures due to low operation lifetime of hydrophobic coating (3-5 years). Accelerated destruction of building materials as a consequence of cracking in waterproofed coating layer is analyzed by Moskvin *et al*. (Moskvin, 1983; Batrakov andSilina, 1977; Batrakov, *et al*. 1977; Solov'ev, 1977)

It has been demonstrated that the highest increase in operation lifetime of material is achieved at bulk water proofing of concretes (Kuatbaev andRoizman, 1972; Baranov, *et al*. 1974).

We believe that kirs and oil sludgescan be applied also in autoclaved foam silicalcite, which is urgent for Kazakhstan due to their wide scale availability. However, water proofing of aerated concrete is not included in the scope of our work, it requires for additional research.

EXPERIMENTAL

The following raw materials were used in our experiments.

Portland cements Vostokcement PTs 500-D20 and Volskcement SSPTs 400-D20 as binders. Chemical and mineralogical compositions of these cements are summarized in Tables 1 and 2.

Table-1. Chemical analysis of cements.

Cement	Oxides, %							
	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	R_2O	SO_3	L.O.I.
Vostokcement PTs 500-D20	20.69	66.13	2.06	4.67	3.46	0.68	1.22	1.09
Volskcement SSPTs400-D20	22.73	65.89	2.27	4.33	2.80	0.60	0.33	1.05

Table-2. Mineralogical compositions of the considered cements.

Cement	Minerals, %			
	$3CaO{\cdot}SiO_2$ (C_3S)	$2CaO{\cdot}SiO_2$ (C_2S)	$3CaO{\cdot}Al_2O_3$ (C_3A)	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ (C_4AF)
Vostokcement PTs 500-D20	59.74	14.87	8.28	14.28
Volskcement SSPTs400-D20	56.35	18.06	6.75	13.55

These cements were selected because they are supplied to West Kazakhstan exactly by the mentioned cement plants.

We developed and applied collagen foam agent obtained by hydrolysis of non-merchantable raw animal skin (KZ Patent No. 25556, Application No. 2011/0882.1 dated 09.08.2011) (Shintemirov, *et al*. 2011).

We applied soft mode of collagen hydrolysis aiming at retention of all amino acids. Saturated solution of calcium hydroxide was used as chemical reagent, which facilitates elimination of several conventional hydrolysis stages. The main advantage of such hydrolysis is that calcium hydroxide is less hazardous in comparison with acids, caustic soda and ammonium.

This work is aimed at establishment of optimum hydrolysis parameters of collagen raw material, providing obtaining of the most complete set of amino acids, increased content of raw protein and solubility in water. Optimum conditions were selected in terms of process duration, reaction temperature, concentration of $Ca(OH)_2$, solution, raw material to chemical reagent ratio.

In the applied experimental layout three hydrolysis parameters were permanent (raw material: $Ca(OH)_2$ ratio, $Ca(OH)_2$ concentration, temperature), and the fourth parameter was variable, time in this case.

Hydrothermal bomb of stainless steel was loaded with 90 ml of tap water, filled with 50 g of collagen chips and 5 ml of 25% solution of $Ca(OH)_2$. The hydrothermal bombs were sealed, fixed in racks of drying oven, the electric drive rotating the bombs was activated and then the oven was switched on. Hydrolysis was performed at 120…125°C. Herewith, excessive pressure of 0.27…0.3 MPa was created inside the hydrothermal bomb. Duration of the process was 2, 3, 4, 5 and 6 hours.

After each reaction cycle the hydrothermal bombs were cooled in running water (quenching procedure applied for synthesis of hydrosilicates), the lid was removed and the content was analyzed. Experiments revealed that under such hydrolysis conditions ($Ca(OH)_2$: raw material ratio 1.9:1 and 120…125°C) the optimum time is 4 h-6 h. Under such conditions collagen raw material was completely dissolved. The obtained hydrolysate was analyzed for content of raw protein, total nitrogen, moisture content and degree of enzymatic hydrolysis. The analyses were performed in R&D Institute of Engineering and Resource Saving. It is established that under such hydrolysis modes (4 h-6 h) the final product is characterized by high amount of raw protein (83%) and degree of enzymatic hydrolysis (78.6…80%). Isoelectric point of the product was achieved at pH = 5.4…5.6.

We determined surface tension of solutions of various concentrations in thermostated cell. Surface tension isotherms are summarized in Table-3.

Table-3. Isotherms of surface tension of keratin hydrolysate (Wilhelmy plate method, t = 25°C).

Content, %	**1.0**	**5.0**	**11.0**	**11.5**	**22.0**	**22.5**	**33.0**	**33.5**	**44.0**	**44.5**	**50**
σ, mN/m	558.7	554.2	448.1	446.5	445.9	442.2	339.4	339.2	339.2	338.8	388.8

RESULTS AND DISCUSSIONS

The data in Table-3 demonstrate that the surface tension decreases with increase in surfactant content. However, after reaching 3% the surface tension is stabilized. Probably, this can be attributed to saturation of adsorption layer of double-sided films due to peculiar properties of protein surfactants. This feature of the properties of protein surfactants is exhibited in very slow setting of equilibrium value of surface tension. Slow formation of equilibrium adsorption layer was attributed to diffusion of globular molecules to interface and generation of peptide chain on the surface. Recently it was assumed that the diffusion of molecules to the surface is not the determining factor of setting time of equilibrium surface tension. According to these assumptions protein molecules in adsorption layer can be uncoiled in the form of single portions depending on the type of protein molecule, protein content, medium pH and other factors. The most probable is that long protein molecule is in an intermediate state, being neither completely uncoiled nor completely coiled. Since several layers cannot be formed upon adsorption, adsorption films can retain coiled native molecules. These circumstances explain practically known higher stability of soams of protein solutions in comparison with foams of synthetic surfactants.

It is known that in liquid foams there occur process of film thinning under action of gravity field, capillary pressure (suction into the Plato channels), van der Waals forces. In bubble films various capillary pressures exist, which increase with decrease in bubble diameter. Therefore, gas is diffused via liquid walls from smaller to bigger bubbles. The gas diffusion transfer should occur slowly, not influencing on total amount of foam, since variation of the total volume indicates at breakage of bubble walls. Form here it follows that in order to decrease has transfer from smaller bubbles to bigger ones it is required to increase the film viscosity. This is aided by various additives which form complexes of various composition with main foam agent, mainly due to formation of hydrogen bonds and interaction of long hydrocarbon chains. Such interaction increases cohesion of molecules in adsorption layer, strongly decreases surface tension of the solution, increases Gibbs elasticity modulus and increases shear viscosity. Such additives are foam stabilizers and act in minor concentrations.

Highmolecularstraight-chaincompoundswithdirect Для стабилизации белковых пенообразователей, как наиболее эффективные, предложены высокомолекулярные соединения с прямой углеводородной цепью (sodium alginates, polyoxides, ceragenins, carboxymethyl cellulose and

others). Such additives create strongly structured adsorption layers and films, providing retention of high bulk of liquid in films.

We selected carboxymethyl cellulose (CMC) as stabilizer - simple ether of cellulose and glycolic acid, $[C_6H_7O_2(OH)_{3-x}(OCH_2COOH)_x]_n$.

Another stage of our research was determination of the influence of the obtained foam agent on cement curing time, since it is known that CMC is applied for adjustment of this parameter (mainly increase in curing duration and plasticity of concrete mix).

The experiments were performed according to regular procedure (Vicat apparatus) with the only exclusion that foam agent solution of preset concentrations were used instead of tempering water.

It was discovered that our developed foam agent slightly increased both the initiation and the completion of curing of cement paste. For instance, the curing initiation increased by 5 min and 15 min, which equals to 1.5% and 4.7%, respectively. Cement curing completion increased by 10 min or 4.0%. This probably can be attributed to experimental error, since State Standard permits deviations in deepening of cement needle (Vicat apparatus) by about 1 mm.

Thus, aiming at decrease in cement curing duration we decided to add electrolyte salts to our foam agent, which would not impair foaming ability and foam stability, and reduce cement curing duration.

The obtained data on foam expansion ratio and foam stability made of agent with CNN, $Ca(NO_2)_2$ evidence that these additives are more efficient than $NaNO_2$.

It follows from the experimental data that addition of electrolyte salts to the considered foam agent improves foam stability. These data agree with the data by Trapeznikov, where it is demonstrated that metal salts interact with main foam agent, and highly dispersed colloidal particles penetrate into the film middle part, formstructure, preventing liquid drain ("seals' the Plato channels), as well as form insoluble salts of organic acids (Trapeznikov 1974).

The more thoroughly studied additive to concrete, characterized by multifunctional action, that is, compacting structure of cement stone, increasing strength of concrete and passivating surface of steel reinforcement, is calcium nitrite-nitrate (CNN).

CONCLUSIONS

a) We developed protein foam agent on the basis of collagen raw material. Collagen should destructed in soft mode at $Ca(OH)_2$ content of 2.0-2.5% and temperature of not higher than 120…125°C. Such hydrolysis mode provides complete retention of amino acids and break of disulfide groups (–SH), which leads to intensive protein foaming.

b) The highest foaming ability of the considered agent is achieved at pH 5.80…5.87. Foam stability increases up to several hours as a consequence of addition of non-ionogenic or ampholytic high molecular surfactants to main foam agent. Additives of this family create strongly structured adsorption layers and films which retain high bulk of liquid in film. We propose the use of polyoxyethylene with molecular weight of higher than 1 million and carboxymethyl cellulose (CMC) with substitution degree higher than 0.8 and polymerization degree higher than 500 as such stabilizing additives.

c) It is established that duration of curing upon production of foam concrete on the basis of protein foam agent can be reduced by addition of calcium nitrite–nitrate. Addition of these salts reduced cement curing duration by 35-65 min, as well as increased foam stability, which can be attributed to additional swelling of protein as a consequence of weakening of intermolecular bonds in the protein structure. Site of connection of salt cations to protein are primarily lateral amino and carboxyl as well as hydroxyl groups.

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