

Results of a Study on Obtaining of the Humic Containing Plasticizers and Their Influence on the Physic-Mechanical Properties for the Cement and Concrete Mixtures

Radnaasediin Sanjaasuren¹, E. Nordov¹, Ts. Erdenebat¹, S. Norjinbadam¹

¹Research Centre of Chemistry and Technology for New Materials, Faculty of Chemistry, National University of Mongolia, Ulaanbaatar, Mongolia, rsanjaas@yahoo.com

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INTRODUCTION

In the modernization of the technology on concrete the important significance has physical chemistry and colloid chemical ideas about mechanism and to the kinetics of the processes of structure formation in the dispersal systems and questions on the influence of different chemical additives, regulated performance properties of concrete. The chemical additives of the organic and inorganic origin, which are introduced into the composition of concrete they contribute to a change in the kinetics of forming of micro-, the macrostructure concrete mixtures due to the adsorptive modification of hydrated phases, formed in the initial setting time and hardening of the binding materials, decrease water-requirements, increase mobility and fluidity of concrete mixture, increase frost resistance and strength indices of concrete.

In recent years, for purposes of the modernization of the technology of concrete the new chemical additives superplasticizers, which are actually surface-active synthetic polymeric substances, widely are used. The countries of superplasticizers, in the industrially developed countries of superplasticizers obtain, in essence, from the individual chemical substances, such, as naphthenic acid, sulfonated naphthalene, melamine-formaldehyde oligomers, polycarboxylates, in connection with which, the cost of these supers-plasticizer is sufficiently high, which limits their uses in practice on a wide scale.

For the Mongolia when, almost they are absent the production of chemical substances, the development of the method of obtaining the plasticizers of high efficiency on the basis of natural organic raw material has great practical value for the production of concretes of different designation. By the purpose of this work is the experimentally substantiation of the method of obtaining the strongly acting plasticizer from the oxidized brown coal high the content of humic substances.

2. MATERIALS AND METHODS

The highly oxidized brown coal of Mongolia served as the starting material of experiment. The proximate analysis of the all-level sample from Baga-Nuur coal deposit face layer as oxidized brown coal, used in this work showed that the output of volatile substances composed about 50,0%, ash content -15,0%, humidity 11,3%. They composed

the element composition of all-level sample (to the combustible mass): C 65,34%, N 4,62%, N 1,27%, O 28,47% (by the weight difference).

The content of the humic acid, extracted by 1% solution of NaOH from this test composed approximately - 60% on the initial dry coal. With the well-known method of obtaining the sulfur-coal cationites on an industrial scale the sulfonation is achieved by an action of the concentrated sulfuric acid or by 20% solution of oleum. In this work for the sulfonation of the humus substances of brown coal was used, on an example of Kulgrena*, soft method sulfonation with the application of the sodium salts: NaHSO₃, Na₂SO₃.

Presence of different functional groups in (- SO₃²⁻, COO⁻, CH₃, CH; OH, SO²⁻, C=C⁻, > C=O and other) for the end product were studied by the method of IR spectroscopic studies.

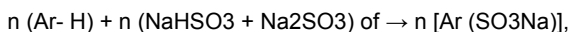
A quantity of chemically bound SO₃ in the end product they were determined by the Eshka method and the average content SO₃ in it was equal to 4,5-4,8%. The influence of the end product of synthesis sulfohumic formaldehyde condensate, in abbreviated form as SHFC on the kinetics structure formation of cement test were studied with the aid of conical plastometer of the construction of MSU. The effects of dosage SHFC on the setting time and after spreading cement test, and also water requirements and the strength of the concrete mixtures were studied by standard methods.

3. RESULTS AND DISCUSSION

It is established that the most suitable time of the process of the sulfonation of the oxidized brown coal (OBC) should be considered 12-14 hours, at a temperature of 120-130°C. The most rational quantity of components, for reacting of sulfonation and polycondensation were as following weight percent: OBC 14,75; Sodium sulfite 3,68; Sodium hydrosulfite 7,37; Formaldehyde 0,48; H₂O the rest.

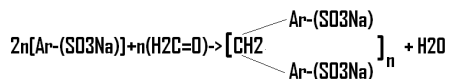
The proximate scheme of the reactions for obtaining sulfohumic-formaldehyde condensate it is possible to describe as follows:

1. Stage of the sulfonation:



where Ar - is the aromatic nucleus of humus substances in OBC.

2. Stage of polycondensation with formaldehyde:



Studies of surface activity $\bar{\delta} = f(C_{\text{SHFC}})$ showed that the surface tension of aqueous solutions SHFC gradually is reduced and with $C_{\text{SHFC}} \sim 09\%$ the surface tension of water it decreases to $\sim 68 \text{ erg/cm}^2$ (with the future with the increasing of the concentration of aqueous solution SHFC surface tension it barely changes).

The dependence of the kinetics of the increase of the plastic strength (rheological characteristic) of cement test on the dosage of additive SHFC (%) is represented in Fig.1

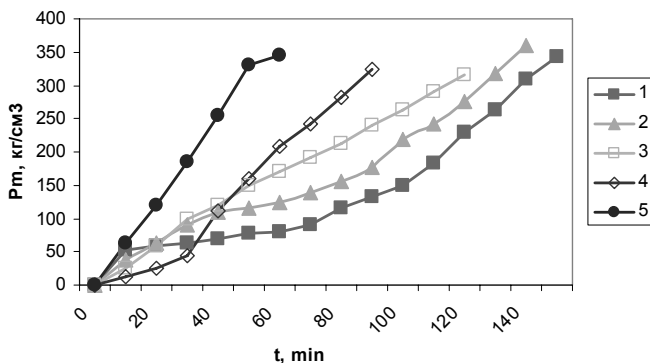


Figure 1. Dependence of the increase of the plastic strength of cement test on the dosage of additive SHFC (%). 1 without the additive it is; 2 0,1% of SHFC; 3 0,9% SHFC; 4 1,5% of SHFC; 5 0,5% of SHFC.

It is evident from Fig. 1 that during 10-15 minutes from the beginning of mixing with the concentrations of the additive SHFC=0.1, 0.9, 1.5 values of plastic strength are lower than in the system without the additive SHFC; beginning 30-40 minutes in the given systems it is observed the acceleration of an increase in the plastic strength in comparison with the system without the additive. When the concentration of addition SHFC =0,5%-Pm is noticeably more than in model without the additive SHFC.

Table 1, presents data on testing of the influence SHFC of lignosulfonate of sodium (obtained by us) and number of imported plasticizers on the strength indices of concrete mixtures.

Table 1. Results of the tests of influence SHFC, LST- SC and imported plasticizers for the concrete pressure strength*

Type of additives	Cement, kg	Sand, kg	Gravel, kg, 5-10 MM	Gravel, kg, 10-20 MM	Dosage of additive, g	Water, kg	w/c	Compression strength, 28 day, mPa
Control	3,6	4,6	4,7	4,7	0,0	1,16	0,30	32
SHFC	3,6	4,6	4,7	4,7	33	0,97	0,27	59
LST-SC	3,6	4,6	4,7	4,7	33	0,97	0,27	68
LS Russian	3,6	4,6	4,7	4,7	33	0,97	0,27	74
LS Chinese	3,6	4,6	4,7	4,7	33	0,97	0,27	74

*Study was conducted by cubes of 100x100x100 mm, aqueous storage with the standard conditions; SHFC ~0,91% of the weight of cement. It is evident from Tabl.1 that the chemical products obtained by us LST- SC, SHFC increase the strength of concrete 1,8-2,1 in comparison with the strength of concrete without the additive. The strength of concrete with the additives SHFC is approximately on 10 mPa lower than with the use of

imported LST, but this fact apparently related with that circumstance that this dosage of additive for SHFC is not optimum, and also imported plasticizers have more complex composition in the plan of the content of additional chemical constituents.

4. CONCLUSIONS

1. Shown the possibility of obtaining sulfohumic - formaldehyde condensate, by being appeared as surfactant anion, from the oxidized brown coal with the high content humic containing of products by their sulfonation by the mixture of sulfites of sodium ($\text{Na}_2\text{SO}_3 + \text{NaHSO}_3$) and subsequent polycondensation with formaldehyde with the relatively soft conditions.

2. The infrared-spectroscopic studies SHFC showed that in this end product are contained such functional groups, as $-\text{COO}^-$, SO^{2-} , $-\text{OH}$, $-\text{SO}_3^{2-}$, and structural elements as $=\text{CH}-$, $-\text{C}=\text{C}-$, $-\text{CH}_2-$, $-\text{CH}_3$.

3. SHFC, obtained by us they are characterized by high surface activity and adsorptivity on the surfaces of the finely dispersed particles of the basic cement minerals (C_3A , C_4AF).

4. Tests on the influence SHFC on the rheological, physic-mechanical properties of cement test and concrete mixtures showed that its application in the technology of concrete of the described

- a. to decrease the water-required in concrete 15-20%;
- b. increases the mobility of cement test and concrete to 10 times;
- c. to increase the strength of studied test and concrete 1,5-1,8 times.

5. It is established that [SGFK], obtained from the oxidized brown coal, which are the withdrawal of coal industry, satisfy basic technical requirements by that presented to the highly active plasticizers of group of chemical additives to the technology of concrete.

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