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THE FORECAST OF DURABILITY OF POLYMER CONCRETES BASED ON LIQIUID RUBBERS WITH THE USE OF THERMOFLUCTUATION APPROACH TO DESTRUCTION AND DEFORMATION OF THE SOLIDS

Problem statement. The aim of the present paper is to perform the forecast of durability of rubber polymer concretes using thermal fluctuation approach to destruction and deformation of the solids.

Results and conclusions. The analysis of the results of researches on determination of rubber polymer concrete durability is performed at matrix level on introduction of the system of accelerators, technological active additive, and various types of fillers in the structure of the matrix.

Keywords: durability, thermal fluctuation method, rubber polymer concrete.

Introduction. Nowadays, the problem of building structure durability is one of the most topical problems. It is known that rubber polymer concretes have high strength and chemical resistant to aggressive mediums, but they lose their strength and rigidity

under the action of elevated temperature. As a result, the durability of structures made from polymer concretes decreases. That is why, the forecast of temperature durability of the structures made from rubber polymer concretes is essential.

1. Thermal fluctuation approach to destruction and deformation of the solids. To determine the durability, we apply thermal fluctuation approach to destruction and deformation of the solids developed by S. N. Zhurkov [1]. The distinction of the method is that it allows one to determine any one of durability boundaries (temporal, force, temperature) in a wide range of interrelated parameters.

In the present paper, following relationships obtained by S. N. Zhurkov and V. P. Yartsev [1, 2] are used:

$$\tau = \tau_m \cdot \exp\left[\frac{U_0 - \gamma\sigma}{R \cdot T}\left(1 - \frac{T}{T_m}\right)\right], \quad (1)$$

$$\sigma = \frac{1}{\gamma}\left[U_0 - \frac{2.3 \cdot RT}{1 - T / T_m}\lg\frac{\tau}{\tau_m}\right], \quad (2)$$

$$T = \left[\frac{1}{T_m} + \frac{2.3R}{U_0 - \gamma\sigma}\lg\frac{\tau}{\tau_m}\right]^{-1}, \quad (3)$$

where σ, T, τ are strength, MPa, temperature, ^{0}K, time before destruction, sec; R is the universal gas constant; γ is the force, structural-mechanical factor; U_0 is the energy of activation of destruction; T_m is the ultimate temperature; τ_m is the minimum durability under any load or without load.

To determine the time before destruction of the samples, we applied formula (1). Formulae (2), (3) are obtained from (1). To predict the boundaries of normal operation of material, it is essential to determine constants τ_m, U_0, γ and T_m, entering into formulae (1)—(3).

2. Statement of the experiment and technique of durability constant determination. To determine durability constants, we produced the samples of the following composition (percentage by mass): liquid rubber — 11.0, hardening group components — 9, filler (crushed sand, fly ash) — 11.0, sand of Volsky sandpit — 23.0, granite crushed stone — 46.0. The varying parameters are components at the level of matrix (hardening group components) and binder.

Sample tests were performed taking structural model in the form of cantilever beam, whose free end was loaded, the following normal stresses being produced in constraint: 5.69; 6.04; 6.4 MPa. The temperature was from 60 to 105 ^{0}C. We also determined the time of destruction τ, sec. The plot for three stress levels was constructed in coordinate system «$1/T$- $\lg\tau$» (Fig. 1). To obtain one point on the plot, 3 samples in

the form of beam of sizes 30×60×700 mm. Using interpolation technique, we constructed straight lines. The lines (see Fig. 1) intersect in the point with coordinates ($1/T_m$-lg τ_m).

In order to obtain the rest two constants U_0 *a*nd γ, let us determine the value of effective energies of activation from equation [3]:

$$U(\sigma) = \frac{2.3 \cdot R\Delta \lg \tau(\sigma)}{\Delta 1/T}. \quad (4)$$

Let us next to construct a plot in coordinate system «σ-U». This plot is a straight line (Fig. 2). This straight line intersect ordinate U in point (0; U_0). The inclination of the straight line to the X-axis forms angle α whose tangent is constant γ = tg α (Fig. 2).

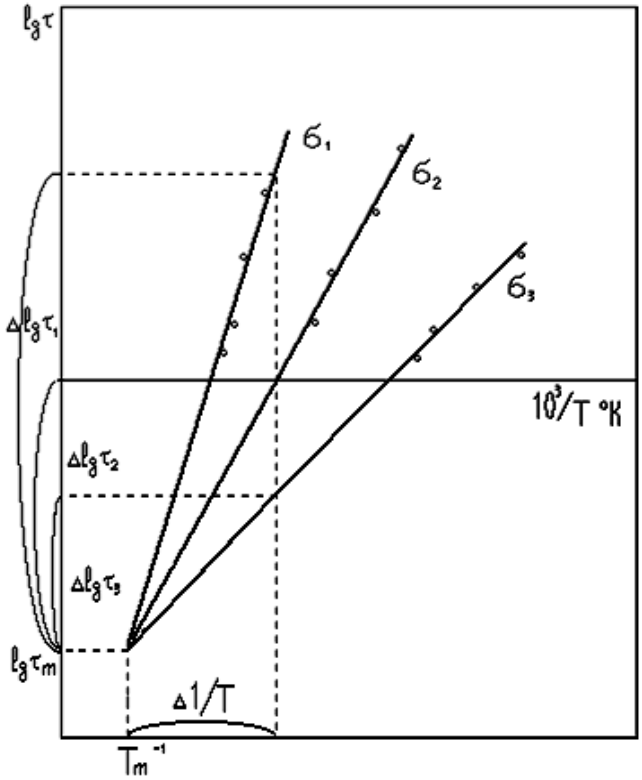

Fig. 1. The scheme for determination of $\Delta \lg \tau_1$, $\Delta \lg \tau_2$, $\Delta \lg \tau_3$ and $\Delta(1/T)$

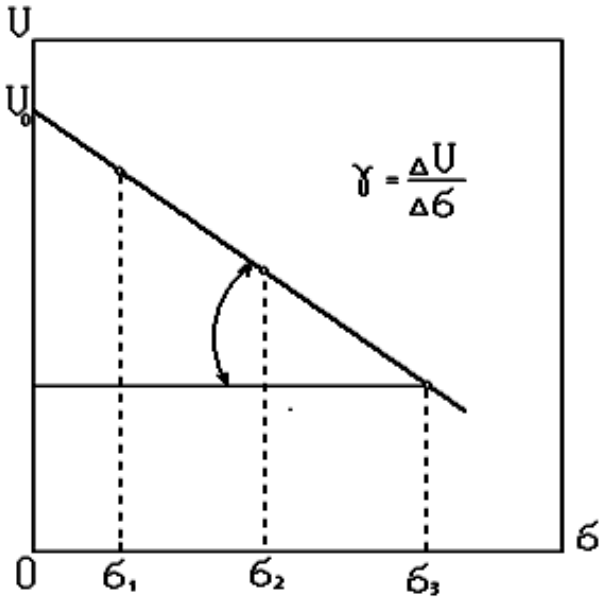

Fig. 2. The scheme for determination of constants U_0, γ

Substituting obtained constants τ_m, U_0, γ and T_m into (1…3) and setting parameters σ, T, τ make it possible to forecast structure durability.

3. The results of experimental studies. Table 1 presents constants determined experimentally for the samples of different compositions.

Table 1

Durability constants for different compositions of rubber polymer concrete

The number of composition	Polymer	Hardening group components	Filler	U_0, kilojoule/ mole	$\lg \tau_m$, sec	γ, kilojoule×mm / (mole N)	$10^{-3} T_m$, K^{-1}
1	Rubber СКДН-Н*	Sulphur, tiuram, zinc oxide, calcium oxide	Sand, crushed stone	293.9	–1.6	25.7	2.15
2	Rubber ПБН	Sulphur, tiuram, zinc oxide, calcium oxide	Sand (specific surface 300 m^2/kg), crushed stone	388	–1.33	40.0	2.2
3	Rubber ПБН	Sulphur, tiuram, zinc oxide, calcium oxide	Sand (specific surface 100 m^2/kg), crushed stone	406	–1.33	44.0	2.18
4	Rubber ПБН	Sulphur, tiuram, zinc oxide, calcium oxide	Fly ash (specific surface 350 m^2/kg), crushed stone	402	–1.2	42.5	2.2
5	Rubber ПБН	Sulphur, tiuram+captax, zinc oxide, calcium oxide	Fly ash (specific surface 350 m^2/kg), crushed stone	419	–1.02	45.4	2.22
6	Rubber ПБН	Sulphur, tiuram, active additive ВЦ-20П, calcium oxide	Fly ash (specific surface 350 m^2/kg), crushed stone	411	–1.05	43.9	2.22

Annotation: *compared ratio (obtained by T.V. Makarova [4]).

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4. The example of determination of durability constants. Let us consider the example of determination of durability constants of composition N 2 (see Table 1).

Using the technique described above we obtained experimental data presented in Table 2.

Table 2

Experimental values of stresses, temperatures, and time before destruction of composition N 2

Stress σ, kN/cm^2 (MPa)	Temperature T		1000/K	τ of destruction		lgτ
	^{0}C	K		min	sec	sec
0.569 (5.69)	75	348	**2.87**	438	26280	**4.42**
	78	351	**2.85**	152	9120	**3.96**
	70	343	**2.92**	915	54900	**4.74**
	96	369	**2.71**	18	1080	**3.03**
	85	358	**2.79**	95	5700	**3.76**
	105	378	**2.65**	4	240	**2.38**
0,604 (6,04)	75	348	**2.87**	64	3840	**3.58**
	72	345	**2.90**	85	5100	**3.71**
	70	343	**2.92**	260	15600	**4.19**
	66	339	**2.95**	391	23460	**4.37**
	65	338	**2.96**	635	38100	**4.58**
	95	368	**2.72**	6	360	**2.56**
	84	357	**2.80**	48	2880	**3.46**
0,640 (6,40)	65	338	**2.96**	200	12000	**4.08**
	60	333	**3.00**	210	12600	**4.10**
	67	340	**2.94**	174	10440	**4.02**
	80	353	**2.83**	15	900	**2.95**
	70	343	**2.92**	33	1980	**3.30**
	88	361	**2.77**	7	420	**2.62**
	78	351	**2.85**	30	1800	**3.26**

To obtain physical constants, we processed experimental data in coordinates lgτ-1/T (Fig. 3).

The coordinates of the intersection point of the pencil of lines corresponding to the different level of stress are constants ($1/T_m$; lgτ_m):

$$1/T_m = 2.2,$$

$$T_m = 455 \text{ K},$$

$$\lg\tau_m = -1.33,$$

$$\tau_m = 0.047 \text{ sec.}$$

Using formula (4), we determined the values of effective energies of activation U for each level of load and plotted σ versus U (Fig. 4).

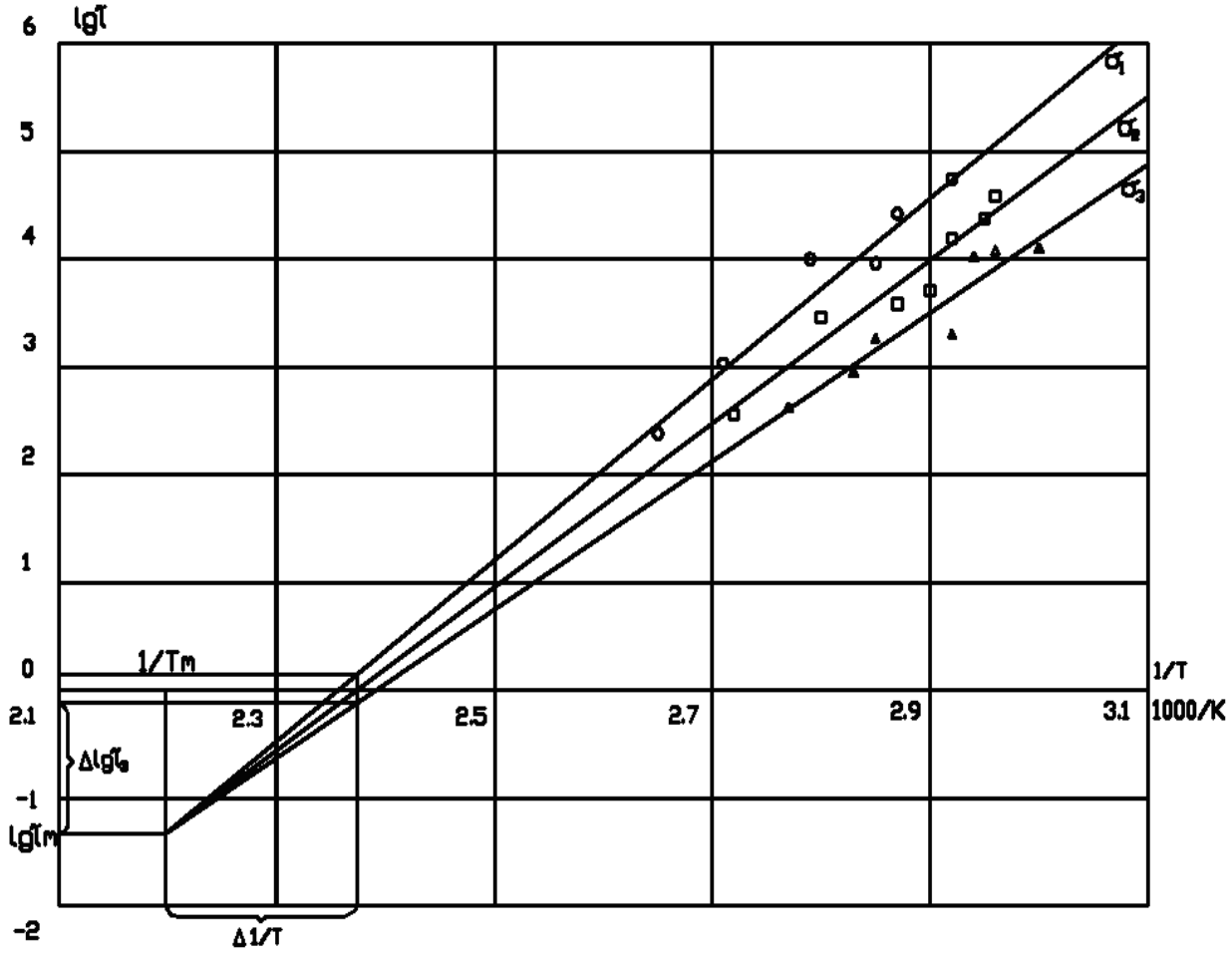

Fig. 3. The relationship between temperature and durability of rubber polymer concrete of grade ПБН at σ_1 = 5.69 MPa, σ_2 = 6.04 MPa, σ_3 = 6.4 MPa

The intersection of the line «σ_1–σ_2–σ_3» with ordinate U corresponds to the point (0; U_0). The tangent of the angle of the slope α of the line «σ_1–σ_2–σ_3» to the X-axis is γ:

$$U_0 = 388 \text{ kilojoule/mole;}$$

$$\gamma = 0.400 \text{ kilojoule}\cdot\text{cm}^2/(\text{mole}\cdot\text{N}) = 40{,}0 \text{ kilojoule/(mole}\cdot\text{MPa).}$$

The constants for the samples of other compositions presented in Table 1 were obtained in a similar way.

To analyze the results of the study, let us substitute the constants obtained into formula (1). Let us specify the stress $\sigma = 6$ MPa and temperature $T = 85\ ^0$C and determine time before destruction. Similarly, we obtain time before destruction of the samples for all specified parameters (see Table 3).

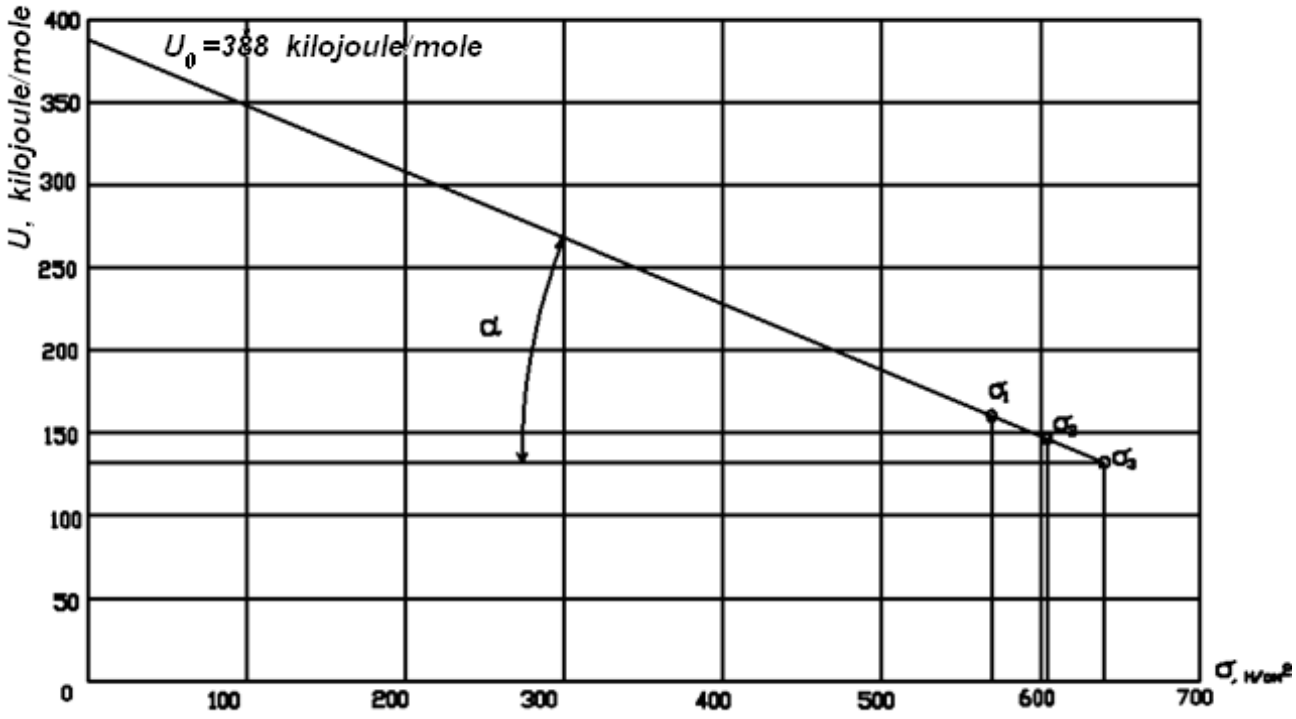

Fig. 4. σ-U relationship for determination of γ

Table 3

Time before destruction of the samples
of various compositions of rubber polymer concrete

Number	Polymer	Hardening group components	Filler	τ, minutes
1	Rubber СКДН-Н	Sulphur, tiuram, zinc oxide, calcium oxide	Sand, crushed stone	20
2	Rubber ПБН	Sulphur, tiuram, zinc oxide, calcium oxide	Sand (specified surface 300 m^2/kg), crushed stone	31
3	Rubber ПБН	Sulphur, tiuram, zinc oxide, calcium oxide	Sand (specified surface 100 m^2/kg), crushed stone	28
4	Rubber ПБН	Sulphur, tiuram, zinc oxide, calcium oxide	Fly ash (specified surface 350 m^2/kg), crushed stone	36

End of Table 3

Number	Polymer	Hardening group components	Filler	τ, minutes
5	Rubber ПБН	Sulphur, tiuram + captax, zinc oxide, calcium oxide	Fly ash (specified surface 350 m^2/kg), crushed stone	41
6	Rubber ПБН	Sulphur, tiuram, active additive ВЦ-20П, calcium oxide	Fly ash (specified surface 350 m^2/kg), crushed stone	41

Conclusions.

1. Polymer concrete having liquid rubber of grade ПБН in its composition (composition 2) has higher durability compared to the polymer concrete based on liquid rubber of grade СКДН-Н (composition 1).

From our standpoint, this is because ПБН has mixed structure (it contains 35…40 % of 1.4 trans bonds, 25…30 % of 1.4 cis bonds, 28…35 % of 1,2-vinyl bonds, and 4…10 % of benzene end groups $C_6H_5CH_2$), in contrast to СКДН-Н which is comprised predominantly of 1.4 cis bonds (75.5 %). During the oxidation of material double bonds of the main chain (cis-1.4-) are more active with respect to oxygen than double bonds of side vynil 1.2-groups. This is due to the fact that formation of thermal fluctuation bireaction centres because of the split in the main chain and in 1.4 cis bonds of monomer is more preferable at the expense of excess of kinetic thermal fluctuation energy of fluctuations of main chain than at the expense of torsion movements of vinyl groups whose energy is deficient for transition in the state of reaction [3].

Furthermore, higher indices of durability of rubber concrete based on liquid rubber of grade ПБН are connected with the fact that cis-1.4 bonds, trans-1.4 bonds, and vinyl 1.2 bonds predominate in their composition, which results in the increase of induction period of three-dimensional polymer formation and increase of double bond conversion level.

2. Polymer concrete which contains the system of accelerants «captax+tiuram» in its hardening group (composition 5) is more durable than polymer concrete whose hardening group consists only of tiuram (composition 4).

In our standpoint, this is because captax has alkaline character. In combination with tiuram this provides a synergistic result, i.e. tiuram and captax increase the activity of each other. Thermal fluctuations do not result in destruction of the chain because tiuram and captax fix the chain and encourage additional vulcanization.

3. Polymer concrete with active additive ВЦ-20 П in hardening group (composition 6) has higher durability than polymer concrete with zinc oxide in hardening group (composition 4).

In our opinion, this is because the introduction of technological additive ВЦ-20П assists in reduction of the number of heat-nonresistant polysulphide linkages, formation of the optimal amount of cross-linkages with lower level of sulfidity, which increases heat resistance and durability of the structure.

4. Polymer concrete filled with fly ash (composition 4) is more durable than polymer concrete filled with fine sand (composition 2). From our standpoint, this is attributed to the chemical composition of fly ash. Fly ash has higher specific surface and adhesion strength at the boundary of phases «polymer-filler».

The results of the study enabled us to select optimum compositions with respect for temperature, temporal and force durability (composition 5 and 6).

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