Testing of Binders Toxicological Effects

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Abstract. The article presents the results of a study of the toxicological effect of binders with different compositions on the vital activity of plant and animal test-objects. The analysis of the effect on plant cultures was made on the basis of the phytotesting data. The study of the effect of binders on objects of animal origin was carried out using the method of short-term testing. Based on the data obtained, binders are ranked according to the degree of increase in the toxic effect: Gypsum → Portland cement → Slag Portland cement. Regardless of the test-object type, the influence of binders is due to the release of various elements (calcium ions or heavy metals) into the solution. In case of plant cultures, the saturation of the solution with elements has a positive effect (there is no inhibitory effect), and in case of animal specimens - an increase in the toxic effect.

1. Introduction
One of the primary tasks of modern construction, arising in conditions of growing ecological instability of urban areas, is the provision of a comfortable human environment [1].

Modern building composites often contain environmentally unsafe components of organic and inorganic nature. Such substances can have a negative impact on living systems, due to changes in biotic relationships between organisms, the biological cycle, the decline in the number of living organisms and the reduction of biodiversity [2-6].

Among the main binders widely used in the production of building composites are portland cement, Slag-Portland cement and gypsum. The necessity of using these components in the conditions of vital activity of organisms of plant and animal origin sharply raises the task of assessing their impact on the surrounding ecosystem. This is due to the fact that such substances can have a negative impact on living systems due to changes in biotic relationships between organisms, the biological cycle, the decline in the number of living organisms and the reduction of biodiversity [7-14]. In connection with this, the aim of the work was to study the toxicological effect of binders in relation to the basic test-cultures of plant and animal origin.

2. Materials and methods
Cement CEM I 42.5H, CEM III 32.5N, gypsum G-5 B-II were used as the test-objects for study. For the studies of this binders a normal density paste-mixture was formed. The samples were then hardened under normal conditions. The toxicity of substances was evaluated using biotesting techniques that allow detecting the toxic reactions of various sensitive test systems for lethality,
mutational variability, stress response, etc. [15-18]. The toxicity of a material in a work is understood as its property to cause death or pathological changes in organisms [19, 20].

2.1. Substantiation of hazard class of materials on toxicity

The technique is to measure the intensity of germination of the seeds roots of testing cultures (cereals) placed in the aqueous extract of the studied materials. As a model test culture oat seeds were used, characterized by stable germination (at least 95%) and reproducibility of the data compared to the seeds of other cultures.

The test samples of hardened binders were ground to a coarsely dispersed state. Then 10 g of samples were placed in volumetric flasks and filled with distilled water in a ratio of 1/10, stood at room temperature for three days. At the end of the time, the flasks were shaken for 2 hours and filtered. Work solutions were obtained by diluting the obtained extract with distilled water in a ratio of 1/10, 1/100, 1/1000 and 100%. Oat was chosen as the test-culture, which is due to more stable and reproducible data compared to other cereals (preliminary germination not less than 95%). The seeds of the test culture were germinated in Petri cups, distilled water served as a control medium. At the bottom of each bowl with filter paper 25 seeds of oat were placed. All bowls were closed with an aqueous extract of the test material (5 ml each), with distribution of the solution throughout the bottom of the bowl. After preparation, the samples were placed in a thermostat for 7 days.

After the specified time, the control measure of the length of the roots of the test-culture seeds was carried out for the control and test samples. The object of measurement for each seed was the root of maximum length.

The visual evaluation of the test samples was carried out independently of the calculation method, since in the calculation method only the root length of the most active oat seedling is taken into account, which does not give a complete idea of the phytotoxicity of the studied material.

The phytotoxic effect is determined by comparing the results of the control and experimental seeds of the test culture. As a quantitative evaluation of the phyto-effect, the calculated value Et (the inhibitory effect) is calculated by the formula:

\[ E_t = \frac{L_k - L_{ow}}{L_k} \times 100\% \]  

where \( L_k \) is the average root length of the test culture in the control solution (mm), \( L_{ow} \) - the average length of the roots of the test culture in the test (working) solution (mm). In this case, the phytotoxicity limit for living organisms is taken as 50%.

2.2. Biotesting when Daphnia Magna is used as a test object

Biotesting was carried out by a short-term method. It is based on determining the survival rate of daphnia when exposed to toxic substances contained in the aqueous extract of the test samples compared to the control. Because of the highest sensitivity to toxicants of different nature, cladoceran of the genus Daphnia were used as the test-object.

To prepare the aqueous extract distilled water with pH = 7.27 was used, which was previously held for 48 hours in an open bowl and saturated with oxygen by means of an aerator for the aquarium. For the preparation of aqueous extracts, cube samples with size 2 cm were weighed and filled with distilled water in a ratio of 1/10 by weight. The samples were kept at room temperature for 10 days. After that, the solid phase was separated by filtration. The pH of the obtained filtrate was determined using an OYSTER-10 instrument and diluted at 1/1 and 1/3, then biotesting was carried out.

Planting of the synchronized culture of daphnia into vessels was carried out as follows: using a glass tube, young (newborn) daphnia were caught and placed in a container with the test fluid and diluted three times in an amount of 6 individuals in each container and exposed for 96 hours.

The surviving daphnia were counted at 1, 24, 48, 72, and 96 hours. Observations were made hourly in the initial period of the experiment (up to 4 hours), on the following days 1-2 times a day. During the observation, the surviving and dead organisms were counted, and the percentage of surviving
individuals was calculated. The time of death of the cladocerans was noted after the onset of immobility (daphnia lie on the bottom of the glass, swimming movements are absent and do not resume when the flask is slightly moved). Daphnius were not fed during the experiment.

The percentage of dead daphnia in the test water compared to the control is calculated by the formula:

$$A = \frac{X_c - X_m}{X_c}$$  

where $X_c$ is the average number of daphnia surviving in the control; $X_m$ is the average number of daphnia surviving in the test medium.

3. Results and discussions

3.1. Phytotesting

According to the obtained data, all seeds, regardless of the type of binder acting as a filtrate component in the aqueous medium, are characterized by the presence of a visible stem (Figure 1, 2). The purity of the surface of the sprouted seed is noted. The number of grains without elements of the root system is insignificant in relation to the total number of grains in each of the bowls. Separately, it is necessary to mention the increased amount of darkening on the surface of grains, which is especially noticeable on samples grown on extracts with a slight dilution. In this case, the length of the root, which is a criterion for the toxicity of the material, is significantly different. However, based on a visual assessment, it is impossible to draw an exclusive conclusion that the binders under study have a negative effect on the germination capacity of the culture.

![Figure 1. Seeds germinated in control solution (distilled water)](image)

As a result of assessing the phytotoxic influence on the effect of inhibition of root growth, the following conclusions can be formulated. The minimum inhibition effect has a gypsum binder when used as an initial undiluted extract (Figure 3). Phytotoxic effect has a negative value, which is expressed in an increase in the intensity of growth of roots of the seed. With further dilution of the initial filtrate, the phytotoxicity of the extract is increased.

Similar data were obtained using portland cement. Nevertheless, several atypical results attract attention. When using the initial undiluted filtrate, the inhibition effect is within the limit of toxicity value. With a slight dilution of the initial solution, inhibition of root growth decreases. Further increase in the degree of dilution of the initial system leads to an increase in the phytotoxic effect to the original value.

The following may serve as an explanation of these phenomena. Exposure of gypsum and Portland cement in water leads to the release of calcium ions in the solution as the main elements of the material. Oat is a culture that grows well on soils with a high level of alkalinity. This ensures a good germination capacity when growing in model extracts. An increase in the degree of dilution of the solution leads to a depletion of the solution in terms of reducing nutrients, which is expressed by an increase in the inhibitory effect.
Figure 2. The intensity of seed growth, depending on the type of extract.

Figure 3. The dependence of the inhibition effect on the type and concentration of the binders extract.
The use of portland cement with the addition of slag as an exposure solution leads to other results. The original extract has the maximum toxic effect. Reducing the concentration of the initial filtrate in the solution leads to some (insignificant) decrease in the effect of inhibition. This is due to the fact that this kind of cement contains slags in its composition, the chemical composition of which is characterized by the presence of a significant amount of heavy metals, which is carcinogenic for plant organisms.

3.2. Biotesting
According to the method, solutions based on filtrates of binders were obtained. It was found that the exposure of samples of binders in water leads to an increase in the pH of the solution (Table 1). The maximum value has the solution based on slag Portland cement, the minimum - based on gypsum.

| Type of binder          | pH   |
|------------------------|------|
| Pure water             | 7,3  |
| Gypsum                 | 7,7  |
| Portland cement        | 9,15 |
| Slag Portland cement   | 9,4  |

Cladocerans Daphnia are very sensitive creatures that respond to small changes in the environment. It is obvious that changing the hydrogen index of their stay environment will affect their behavior. Thus, the study of survival of individuals for 4 days confirmed the assumption (Table 2).

According to the data obtained, in most of the extracts from the materials, the mortality of individuals is significantly increased in comparison with the control (aerated tap water). At the same time, for 2 samples 100% mortality occurs on the second day (48 hours).

The maximum survival is characterized by individuals functioning in pure (distilled) water. Even to the last days of measurement, their lethality does not exceed 10%. When using portland cement solution as a living medium for cladocerans its its toxic effect becomes evident: with a small dilution of the initial extract, the absence of survival of the objects is already observed on the second day; dilution of the solution three times ensures a reduction in the level of mortality of individuals in the initial periods, however, complete extinction occurs after the second day.

| Type of solution       | Lethality, % |
|------------------------|--------------|
|                        | Exposure time, h |
|                        | 1  | 14 | 24 | 48 | 72 | 96 |
| Pure water             | 0  | 0  | 0  | 0  | 0  | 10 |
| With extracts of binders | Dilution 1/1 |
| Portland cement        | 0  | 50 | 83 | 100| –  | –  |
| Slag Portland cement   | 0  | 83 | 100| –  | –  | –  |
| Gypsum                 | 0  | 16 | 33 | 50 | 50 | 60 |
| With extracts of binders | Dilution 1/3 |
| Portland cement        | 0  | 16 | 33 | 100| –  | –  |
| Slag Portland cement   | 0  | 73 | 100| –  | –  | –  |
| Gypsum                 | 0  | 0  | 16 | 16 | 16 | 40 |
In the case of using slag portland cement as a carrier medium for obtaining a solution, regardless of the degree of dilution after 1 day, a 100% lethality of the test object is observed.

Exclusion from binders constitutes only gypsum: when using gypsum filtrate solution in small dilution only after 4 days the lethality of individuals exceeds the limit for toxicity values. However, with a greater dilution of the solution to the end of the experiment, more than half of the individuals retain their viability.

The results obtained in the framework of the study shows the presence of substances that exert an acute toxic effect on living organisms in the extracts and, consequently, in the water-soluble part of the materials under study.

4. Conclusion.

The work analyzes binders of various compositions used as a basis for the production of building composites, as well as for the decoration of rooms for various purposes. The influence of the binder type on the toxicity of its filtrate has been analyzed.

By the degree of reduction in the harmful effect (increasing toxicity) on plant and animal test-objects as biological indicators of the purity of the environment, very sensitive to changes in its composition, the materials under study can be arranged in the following order: Slag Portland cement → Portland cement → Gypsum.

The effect of binders on the vital activity of test cultures is due to the release into the solution of elements formed during the hardening of binders. In the case of gypsum and Portland cement, "leaching" of the solution (the yield of calcium ions into the solution) is noted, which provides an increase in the intensity of growth of the roots of the plant. However, in the case of animal test objects, a change in the composition of the aqueous medium results in a decrease in their survival. Nevertheless, when using gypsum stone, regardless of the degree of dilution of the initial extract, the lethality does not exceed the limit value.

The use of slag Portland cement, which contains slag waste, characterized by a high content of heavy metals, has a significant toxic effect, regardless of the type of test culture.

Thus, the results of toxicological studies of binders allow us to optimize approaches to the production of constructional and special materials taking into account modern requirements for environmental safety and biological positivity.

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References

[1] Lesovik V S, Zagorodnjuk L H, Volodchenko A A, Glagolev E S, Sumskoy D A and Kaneva E V 2016 Int. J. of Pharm. and Tech. 8 24868
[2] Strokova V V, Botsman L N and Ogurtsova Y N 2015 Int. J. Appl. Eng. Res. 10(24) 45169
[3] Strokova V V, Zhernovsky I V, Maksakov A V, Solovieva L N and Ogurtsova Y N 2013 Build Materials 1 38
[4] Vasilenko M I, Goncharova E N, Rubanov Y K, Tokach Y E and Shovea E A 2015 Int. J. Appl. Eng. Res. rch. 10 42658
[5] Vasilenko M I, Goncharova E N, Narzev V M, Sokolova Y D and Evtushenko EI 2015 J. of Pharm., Biol. and Chem. Sc. 6 1622
[6] Tokach Y E, Rubanov Y K, Vasilenko M I, Goncharova E N, Evtushenko E I and Kazaryan S A 2014 Res. J. of Appl. Sc. 9 774
[7] Kapusta M N, Kobzev V A and Nelyubova V V 2014 Appl. Mech. Mater. 670–671 412
[8] Nelyubova V, Pavlenko N and Netsvet D 2015 IOP Conf. Ser.: Mat. Sc. and Eng. 96 012010
[9] Fediuk R S, Yevdokimova Y G, Smoliakov A K, Stoyushko N Y and Lesovik V S 2017 IOP
Conf. Ser.: Mat. Sc. and Eng. 221

[10] Pavlenko N V, Strokov V V, Cherevatova A V, Netsvet D D and Miroshnikov E V 2014 App. Mech. and Mat. 496 2383

[11] Kozhukhova N I, Chizhov R V, Zhernovsky I V and Strokov V V 2016 Int. J. of Pharm. and Tech. 8 15338

[12] Fisher K B, Rikhert K, Burianov A and Strokov V 2016 Int. J. of Env. and Sc. Ed. 11 12361

[13] Kozhukhova N I, Zhernovsky I V and Strokov V V 2015 Int. J. of App. Eng.Res. 10 35618

[14] Fomina E V, Strokov V V, Kozhukhova N I and Fomin A E 2016 Ind. J. of Sc. and Tech. 9 95545

[15] Mehrangiz F and Alireza K 2015 Appl. Cat. A: Gen. 491 136

[16] Rede D, Santos H M L M, Ramos S, Oliva-Teles F, Antão C, Sousa S R and Delerue-Matos C 2016 Chem. 159 193

[17] Vannini C, Domingo G, Onelli E, De Mattia F, Bruni I, Marsoni M and Bracale M 2014 J. of Pl. Phys. 171 1142

[18] Krizek D T and Mirecki R M 2004 Env. and Exp. Bot. 51 33

[19] Lomonte C, Doronila A I, Gregory D, Baker A J M and Kolev S D 2010 J. of Haz. M. 173 494

[20] Foghmoes S, Teocoli F, Brodersen K, Klemensø T and Della Negra M 2016 J. of the Eur. Cer. Soc. 36 3441