Research Journal of Applied Sciences 9 (11): 774-778, 2014
ISSN: 1815-932X

Design of New Approaches and Technological Solutions of Obtaining Biocidal Compositions to Protect Industrial and Civil Buildings and Constructions Against Biodeterioration

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Abstract: There was suggested the method of obtaining biocidal compositions from electroplating industry waste by means of biotoxicants concentration. The method includes mixing galvanic sludge with ammonium chloride in stoichiometric proportion, mechanochemical activation of the obtained mix to the size of 0.5-5 μm, the sub-sequent heat treatment in the muffle furnace at temperature 450-500°C, leaching of the obtained sinter with wastewater from the same electroplating plant and of similar composition at at pH≤3, detachment of sediment by filtration and extraction of metals compounds out of the obtained solution by electroflotation method at pH = 8-10. The obtained concentrates were dried and kilned at temperature 650°C to obtain metal oxides. The biocidal properties of the obtained materials were determined by using microfungi of Aspergilius, Pennicillium, Cladosporium genera. The comparative characteristics of microorganisms development on the initial galvanic sludge and on the modified sludge were shown. It was detected that introducing additives, obtained after processing galvanic sludge, contributed to 3 fold reduction of the fouling degree of samples at the average, in comparison with the initial sludge, both by green and by blue-green algae. The optimal concentration of biocidal additive in building mixes was determined and amounted to 1-2%. At this, the physical and mechanical properties of samples did not reduce.

Key words: Mechanochemical activation, leaching, reactivity, bioresistance, fungicidity

INTRODUCTION

Solving the problems in the sphere of improving the biological protection of residence and civic buildings requires organizing the inspections of urban buildings, carrying out examinations, setting-up designated labs for researching the processes of biodegradation and bioresistance of materials, designing programs of preventing biodeterioration in cities and systems of managing biochemical and corrosion processes in construction, providing the appropriate protection of buildings and constructions.

Over recent years there was acquired a lot of information, giving evidence about the destructive effect of microorganisms on building materials and constructions in technogenic environment. In the high humidity areas of residence and civic buildings (in cellars, sanitary facilities, basements, roof drainages, swimming pools, etc.) the microbiological corrosion becomes an important factor, having influence on reliability and durability of building structures. Apart from technical aspect there is also the ecological aspect of the problem. The structures' fouling with microfungi, the growth of bacteria in porous building materials degrades the hygienic conditions in premises.

In building and building materials industry the problem of protecting materials and products against biodegradants is especially topical. One of the most efficient and long-acting ways of protecting building materials and constructions against microbiological affection is the application of biocidal substances. But the underexplored mechanisms of their interaction with building materials and the high adaptation power of microorganisms to the varying environment make the problem of protecting building materials and structures rather complicated and relevant.

The problem of biodeterioration of building materials and products is connected not only with the reduction of buildings and constructions' durability but with the affect of biodestructing substances on the population health. A certain solution of this problem can be presented by using biocidal additives for building materials. Among the

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inorganic antimicrobial systems, the copper, chrome, zinc and silver compounds as well as organotin biocide are used. Among the polymeric compounds the guanidine-based compounds and chloromethyl derivates of aromatic carbons with pyridine are widely used (Schnard *et al*., 2009; Kuehn, 2003; Scherbo and Antonov, 2008; Dergunova *et al*., 2009).

BASIC PARTP

Researchers of the study have carried out the research, aimed at producing biocidal compositions for building materials, constructions and buildings from electroplating industry waste, containing copper, chrome, zinc and nickel compounds.

The object of research was the sludge from galvanizing plant, containing, mg/gk: Zn-46625; Ni-1433; Cu-12750; Cr-23250; Fe-B 20100; Ca-115500; sand, magnesium and sodium carbonates-76781 and wastewater of the same plant, containing the same components, mg/L: Zn 93.3; Ni 2.9; Cu 25.5; Cr 46.5; Fe 40.2. The hydrogen value of wastewater amounted to pH = 2.5.

The purpose of research consisted in obtaining compositions, comprised by heavy metals and having biocidal properties (Zn, Ni, Cu, Cr).

To achieve the set purpose there was developed a technological scheme which includes mixing galvanic sludge with chlorine-containing component in stoichiometric proportion, mechanochemical activation of the obtained mix by grinding it in dry ball mill, leaching the mix with wastewater at pH≤3, detachment of sediment by filtration and extraction of metals compounds out of the obtained solution by Electroflotation Method at pH = 9-10. The ammonium chloride was used as a chlorine-containing component. The stoichiometric proportion of components was determined by chemical equations.

The mechanochemical activation of sludge with ammonium chloride induces the formation of water-soluble compounds in the form of metal chlorides. The supposed chemical nature of the transformation processes of metal sulphides, hydroxides and carbonates into water-soluble chlorides is presented by the following scheme. For sulphides:

$$MeS + 2NH_4\,Cl + 2O_2 \rightarrow MeCl_2 + (NH_4)_2SO_4$$

For hydroxides:

$$Me(OH)_2 + 2\,NH_4Cl \rightarrow MeCl_2 + 2(NH_4)OH$$

For carbonates:

$$MeCO_3 + 2\,NH_4Cl \rightarrow MeCl_2 + (NH_4)_2CO_3$$

Table 1: Dependence of particle size alteration (Fm) on duration of grinding (h)

Duration of activation (h)	The accordance of particle size (D, μm) with the set value of weight fraction (p, %) p (%)	10	30	50	70	90
2	D (μm)	1.22	3.53	9.42	26.4	97.5
4		1.25	3.41	8.54	19.9	81.0
6		1.27	3.73	8.78	21.5	59.7
8		1.13	3.08	7.97	19.6	62.0
10		1.25	2.88	5.99	15.9	55.8
12		1.19	2.73	3.64	13.6	51.3

Table 2: Residual concentration of heavy metals in sediment after leaching

Duration of activation (h)	Heavy metals content (mg kg^{-1}) Zinc	Copper	Iron	Nickel	Chrome
2	15302.4	3844.3	16383.5	1102.3	22725.4
4	13986.8	3412.1	15153.5	993.6	20052.8
6	11114.8	2789.7	10979.0	903.2	14286.2
8	10432.1	2270.7	6845.1	564.4	9375.4
10	5834.4	1374.7	3625.2	375.2	6201.2
12	2265.1	649.1	1865.5	176.9	3162.6

The mechanical activation of the mix was carried out for various periods of time to determine the optimum value of the duration of mechanical action. In the process of mechanical activation in a ball mill, the alteration of particle size of the powder was checked each 2 h with a laser particle analyzer Mikro Sizer 201. The findings are presented in Table 1.

During processing powders in a planetary ball mill, along with grinding, there occur structural changes of the substance. Many defects are formed and the substance becomes reactive. When several reagents are treated, there takes place the interaction between them chemical reaction. In the same way as with solid-phase reactions, going on during thermal activation to initiate a mechanochemical reaction we have to convey the sufficient amount of mechanical energy to the powder (Rubanov and Tokach, 2009).

After activation the mix was leached with wastewater from the same electroplating plant and of similar composition at pH≤3. Thus, the metal ions were moving to the water solution, increasing the concentrations of these metals, solved in the wastewater.

The residual concentration of heavy metals in the galvanic sludge after leaching was determined with an X-ray fluorescent spectrometer ÀRL 9900. The measurement results are presented in Table 2.

The analysis of the obtained findings has shown that at increasing the duration of grinding the degree of fineness altered only slightly. As it follows from Table 2, the size of 90% of the weight fraction of particles reduced from 97.5- 51.3 μm, i.e., by 1.9 times. But the efficiency of extracting metals out of the sludge has increased by≤5 times (Zn-6.8 times; Cu-5.9 times; Fe-8.7 times; Ni-6.3

times; Cr-7.3 times). So, the duration of mechanical treatment, i.e., increasing the input amount of mechanical energy, has a considerable impact on the formation of water-soluble compounds.

In comparison with the initial concentration of metals in the sludge the recovery efficiency made up: Zn-85.2%; Cu B-83.1%; Fe-B88.6%; Ni-B 84.3%; Cr-B 86.4%.

As follows from the obtained findings, under the action of external forces the energy store of the ground material is increased, due to the increase of surface energy which contributes to acceleration of physical and chemical processes. The more impacts are delivered to the particles and the lesser is the interval between the consecutive impacts, the higher is activity and reactivity of the substance.

After detaching the sediment by filtering, the solution was placed into electroflotation chamber 11 large. Floatation process was carried out at current density 50 mA/cm^2 during 20 min after setting pH = 9-10. The pH of the solution was increased by using caustic soda. As a foaming and collecting agent at the flotation metal extraction there were used anionic SAS potassium alkylbenzolsulfonate (sulfonol) in amount of 5 mg/L and potassium xanthogenate in amount of 3 mg for 100 mg of metals ions in solution.

Applying the electroflotation method of extracting metal compounds from solutions is conditioned by its efficiency. By changing the electrical parameters of the process, we can provide the optimum dispersion of air bubbles, without breaking the foam layer. Along with electrode processes, there are bulk chemical reactions going on in an electroflotation unit which results in such phenomena as alteration of nature and solvability of flotation concentrate, dissolving or formation of sediment desintegration of complexing substances, which contributes to the improvement of the process quality (Rubanov and Tokach, 2009).

The obtained foam concentrate was dried and then kilned at temperature 600°C which results in obtaining metal oxides powder.

The biocidal properties of the obtained powders were detected by their effect on various living organisms which most frequently cause biodeterioration of building materials. In the urban environment, the surface of the construction units is constantly attacked by a broad range of such microorganisms. Deterioration of concrete proceeds rather rapidly, if there are favourable conditions for biological agents, characterized by aggressive type of action (chemolytotrophic bacteria and micromycetes) (Vasilenko and Goncharova, 2013; Goncharova and Yurchenko, 2003; Goncharova and Vasilenko, 2013).

These microgerms can leach the mineral matrix which leads to the weakening of the binding building composite. Microgerms-green and blue-green algae, thionic and nitrifying bacteria; microfungi, which cause the most significant damage to building materials (Nick *et al*., 2013; Smith *et al*., 2010; Cuzman *et al*., 2011; De Belie, 2010) were taken from the surface of concrete items and constructions, damaged in the actual conditions of the urbanized environment and used as test systems for examining the biocidal properties of both initial waste and concentrates, enriched with metal oxides.

As biocidal additives there were used the initial galvanic sludge and the metal oxides, obtained after its processing. The experiments were carried out by standard microbiological methods, culturing microorganisms on solid nutrient medium in the presence of initial galvanic sludge and processed galvanic sludge.

The fungicidal properties of the researched materials were determined by using microfungi of Aspergillus, Pennicillium, Cladosporium genera. In all of the variants, the intensity of fungus growth on the surface of the waste amounted to 0. The fungicidity areas (areas of no growth of fungi near the waste, placed in the center of the plate), made up for the mentioned fungi: 5, 53, 52%, respectively.

Processing of waste according to the mentioned earlier technologies, provided the removal of certain components (for example, calcium, potassium, aluminium, sodium, silicium, etc.) and as a result, concentrating of elements, possessing high toxicity to microorganisms (copper, nickel, zinc, etc.). This correlated with the increasing toxicity of the treated waste (Fig. 1).

Through, the example of *Aspergillus* sp. microfungus testing culture it is clearly seen that the fungicidity area is increased from 55% in case with the initial waste to 100% in case with the modified waste (the total absence of the plated fungus growth not only on the surface of the waste but on the whole surface of the nutrient medium).

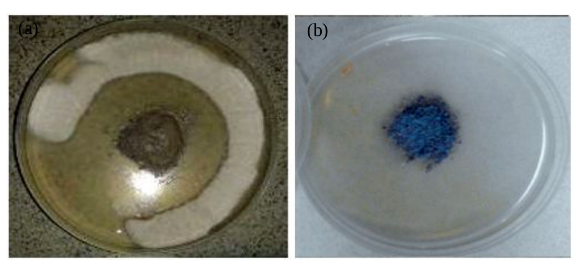

Fig. 1: The fungicidity areas of the researched materials: a) using the initial waste and b) using the technologically processed waste

Table 3: Comparative characteristics of microorganisms development

The tested object	Blue-green algae	Green algae	Nitrifying bacteria	Thionic bacteria	Fungi
Galvanic sludge, initial	-	-	+	+	+
Galvanic sludge after treatment	-	-	-	-	-

+ = Growth of the tested organisms; - = No growth

In case with algae (blue-green and green), unlike with nitrifying and thionic bacteria there was detected the total absence of fungi growth in the presence of both initial waste and the obtained concentrates.

The comparative characteristics of the development of researched organisms on solid nutrient medium in contact with galvanic sludge and the products of its processing according to the described technology are presented in Table 3.

As we see from the resulting data (Table 3), the most sensitive to substances, containing toxic metal compounds were algae which didn't grow on the surface of the nutrient medium on which the samples of the initial waste and of treated waste were placed.

The stronger biostatic effect is typical for the concentrate, obtained after galvanic sludge processing in the presence of which the growth of bacteria and microfungi stopped.

To study the possibility of providing the bioresistance of products, containing the obtained concentrate as a biocidal additive, it was added to the concrete in an amount 1and 2% (by weight).

For the research there were used the cubical-shaped model samples of cement-sand concrete with edge 20 mm (portland cement M400 produced by OJSC «Belgorodsky cement» and sand in the ratio 1:3). The samples were placed into the vessel with liquid nutrient medium for the growth of algae or bacteria or on the surface of solid nutrient medium in the experiments with micromycetes to provide optimal conditions for the growth of the researched organisms, causing biodeterioration of materials (Vasilenko and Goncharova, 2013; Roeselers *et al*., 2007).

After keeping the samples in the given conditions during a certain period of time (up to 30 days), the degree of their fouling with various test-organisms was determined (Table 4 and 5).

As follows from the results, introducing additives, obtained after galvanic sludge processing, contributed to three-fold reducing of the degree of samples' fouling at the average, both in case with green and blue-green algae, so we can make a conclusion that the component obtained from galvanic sludge in the process of new technology is efficient as a biocidal additive in concentration 1-2% which prevents the growth of algae.

Table 4: The degree of algae fouling (%) of concrete material

Samples	Testing culture: Green algae	Blue-green algae
Test samples (without additives)	23.7	36.3
With adding of the processed galvanic sludge (metal oxides concentrate)	6.5	12.0
Content of additive in product: 1 and 2%	6.0	9.5

Table 5: Fouling of composites under the action of filamentous fungi

Samples	Fungus-resistance, point: Method 1	Method 3	GOST characteristics 9.049-91
Galvanic waste (initial)	0	3	Fungus-resistant
Treated galvanic waste (metal oxides concentrate)	0	1	Fungus-resistant
Check sample (without additives)	3	4	Not fungus-resistant

Fungus-resistance and fungicidity of concrete materials were studied in the course of testing for fouling with a filamentous fungus *Aspergillus niger* according to GOST 9.049-91 (1992) by method 1 (material is infested with spores of mold fungi in the water; mold fungi grow only with nutrient substances, contained in the material) and by method 3 (material is infested with spores of mold fungi in the solution of mineral salts with sugar).

Although, method 3 has shown the fouling degree of products, containing the 2% of initial galvanic sludge, amounting to 3 points (mycelia and (or) spores are faintly visible with an unaided eye but are clearly seen under the microscope) by method 1 only the check sample can be considered as failed the fungus-resistance test (fouling degree 3 points) (Nick *et al*., 2013).

Adding the modified waste to the composite increased the fungus-resistance of products fouling degree by method 3 reduced from 4 points in the check sample (the fungi, covering about 25% of the researched surface are clearly seen with an unaided eye) to 1 point at using the obtained metal oxides concentrate (the sprouted spores and slightly developed mycelium are visible under the microscope).

Besides, the building materials were tested for the ultimate compression strength. The check samples with rare exception, virtually did not alter the strength in the course of experiments.

CONCLUSION

Samples, containing the treated galvanic waste in the amount 1% also didn't alter the strength properties of the building material. Samples with 2% of additive, after biodeterioration experiments, apart from not losing strength in cases with all the used organisms, in some cases even improved the strength properties. These facts indicate that applying this biocidal additive in the formula of concrete composite in the mentioned amounts wouldn't have a negative effect on the strength characteristics of concrete products.

IMPLICATIONS

Modification of the electroplating industry waste allows the purposeful production of biocidal substances for building materials and for protection of industrial and civil buildings and constructions against microbiological damage.

ACKNOWLEDGEMENTS

The study is prepared within the framework of performing the project part of state assignment of Assignment No. 14.2406.2014/K and Strategic Development Program of BSTU named after V.G. Shukhov for 2012B2016.

REFERENCES

Cuzman, O.A., P. Tiano, S. Ventura and P. Frediani, 2011. Biodiversity on Stone Artifacts. In: The Importance of Biological Interactions in the Study of Biodiversity, Pujol, J.L. (Ed.). InTech, Rijeka, Croazia, ISBN: 978-953-307-751-2, pp: 367-390.

De Belie, N., 2010. Microorganisms versus stony materials: A love-hate relationship. Mater. Struct., 43: 1191-1202.

Dergunova, A.V., D.A. Svetlov, V.T. Erofeev and V.F. Smirnov, 2009. Microbiological resistance of building materials. Volga District Scient. J., 2: 108-113.

GOST 9.049-91, 1992. Unified system of corrosion and ageing protection. Polimer materials and their components. Methods of Laboratory Tests for Mould Resistance, The Standards Publishing Office, Moscow, pp: 13.

Goncharova, E.N. and E.I. Vasilenko, 2013. Algocenosis of the damaged surface of urban buildings and constructions. Fundam. Res., 8: 85-89.

Goncharova, E.N., V.A. Yurchenko, E.V. Brigada and Y.I. Chaplina, 2003. Microbiological concrete corrosion agents. Ecol. Ind. Russ., 3: 22-24.

Kuehn, T.H., 2003. Airborne infection control in health care facilities. J. Solar Energy Eng., 125: 366-371.

Nick, A., A.V. Heather, S. Ahmad and J. Smith, 2013. Greening and the conservation of stone heritage structures. Sci. Total Environ., 442: 152-164.

Roeselers, G., M.C. van Loosdrecht and G. Muyzer, 2007. Heterotrophic pioneers facilitate phototrophic biofilm development. Microb. Ecol., 54: 578-585.

Scherbo, A.P. and V.B. Antonov, 2008. Biodeterioration of Hospital Buildings and its Influence on Human Health. MAPO., St. Petersburg, Pages: 232.

Schrand, A.M., S.A.C. Hens and O.A. Shenderova, 2009. Nanodiamond particles: Properties and perspectives for bioapplications. Crit. Rev. Solid State Mater. Sci., 34: 18-74.

Smith, B.J., S. McCabe, D. McAllister, C. Adamson, H.A. Viles and J.M. Curran, 2011. A commentary on climate change, stone decay dynamics and the greening of natural stone buildings: New perspectives on deep wetting. Environ. Earth Sci., 63: 1691-1700.

Vasilenko, M.I. and E.N. Goncharova, 2013. Microbiological peculiarities of concrete surfaces' deterioration process. Fundam. Res., 4: 886-891.