AUTO-BINDING PROPERTIES OF DIFFERENT TYPES OF STEELMAKING SLAGS[1]

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Abstract

All the types of dumped ferrous slag (blast furnace, open hearth, electric steel and converter) have manifested unequivocal binding properties. They were studied by wide range of traditional and novel methods self-contained binding properties and physicochemical processes of hydrated slag strengthening up to 6 year s of the samples age. Converter slag showed the best mechanical properties, followed by open-hearth slag, while blast furnace slag displayed the least interesting properties. Its low water and frost resistance render the blast furnace slag under study unusable without the special activation of binding properties. The strengthening of dump ferrous slag is ascribed to the appearance of new amorphous formations, which transform into a stone-like condition over time. The only new crystal formations, detected over a 6-year-long hardening process, were various crystalline carbonates in such small amounts that they cannot be responsible for the materials' highly significant strength (up to 40 MPa) at one year of age. Their long-term properties allow these types of slag to be used as traditional binders for local soils binding, in the preparation of base for highway, airfield runway, dam and building foundation construction applications. More than 300 km of highways with roadbases from these materials have shown excellent performance indices in different parts of Russia, including Siberia and Russian North.

Key words: Dump ferrous slags; Chemical interaction; Strengthening; Amorphous new formations.

PROPRIEDADES AUTO LIGANTES DE DIFERENTES TIPOS DE ESCÓRIAS DE ACIARIAS

Resumo

É possível utilizar vários tipos de resíduos industriais no lugar de materiais de construção naturais (pedra britada, areia, cascalho, etc.) para uso como matéria aglomerante para ligar os solos locais naturais como bases de bases de estradas, pistas de aeroportos, barragens e alguns tipos de fundações. Através de vários métodos modernos de investigação, ficou provado que em resultado de hidratação da escória siderúrgica tem início uma dissolução parcial da parte sólida, formando um sistema de partículas coloidal (sol). Com o aumento da concentração de colóides nos poros, ocorre à formação de um gel amorfo. Este gel se solidifica devido aos vários estágios de sinérese (envelhecimento de gel). Após 28 dias de hidratação, este material atinge resistências à compressão de 1,1 a 3,9 MPa, em 90 dias essa resistência à compressão pode alcançar de 5 a 32 MPa. Com um ano, a resistência deste material aumenta até 40 MPa. Estes novos materiais têm uma alta resistência à imersão e ao congelamento. Estradas urbanas executadas com os materiais mostraram alta performance por mais de 25 anos em diferentes regiões da Rússia, incluindo a região norte e Sibéria.

Palavras-chave: Escória de ferro armazenada; Processo sol-gel; Propriedades mecânicas; Novos materiais de construção.

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1 INTRODUCTION

Dump ferrous slag (DFS) is a metallurgical industry waste producing in large amounts and polluting the nature. The international literature contains many reports on multiple ways of metallurgical slag using. The largest consumers of slag in the form of inert material rather than crushed natural stone, gravel and sand mixtures are road constructors.[1,2] Another widespread application of slag is in the production of Portland cement.[3] Technologies of slag-wool production for thermal and acoustic isolation and for technical glasses are well known. Some authors propose the use of slag to coat environmentally hazardous materials[4] etc. However, most reports so far have concentrated on the use of granulated ferrous slag, a waste product that is not strictly industrial waste but an intermediate product of Portland cement production.

An overwhelming majority of countries that have huge metallurgical industries, however, face a serious problem of what to do with their DFS. All these countries have grave environmental protection problems resulting from the enormous amounts of slag produced, the large areas required to store DFS and the long periods of time over which they have been accumulating. As an example, a single Russian metallurgical plant in Magnitogorsk has accumulated more than 180 million tons of DFS in a nearby dump.

The authors of this paper published [5-7] the results of their investigation into the possibility of chemically strong binding of Electric-Arc Furnace Dust (EAFD) using DFS and of obtaining new construction material. However, no explanation was given of the nature of this slag's binding properties, nor was it reported that practically every type of DFS deriving from metallurgical processes possesses such binding properties, albeit to differing degrees. This paper is dedicated to partially filling in the gaps of our previous publications.

2 RESEARCH GOALS

1. to study the self-contained binding properties of DFS from different metallurgical processes without the addition of any activators;
2. to study the physicochemical processes of hydrated slag strengthening over long periods (e.g., up to 6 years of age).

For the achievement of this goals a wide range of traditional and novel methods of mutually complementary research were used to study the initial slag compositions and their temporal changes during hydration. These methods included the definition of the limit strength under uniaxial compression, temporal changes of moisture and of linear deformation, water and frost resistance, XRD analyses by the powder method, the quantity of bonded water and carbonate content, using TGA and DTA, scanning electron microscopy and chemical analyses (free CaO, SiO_2 , Fe_2O_3 , Al_2O_3 , SO_3 , pH and others), Roentgen-spectral analysis using “Cameca”, “Edax” and “Link-System”, and Laser micro-mass analysis by “LAMMA-1000”.

All the types of slag under study were milled to reach the value of specific surface area of approximately 1000 cm^2/g.

3 EXPERIMENTAL SECTION

The samples of the materials were compacted for 1 min under a 10 MPa pressure in a cylindrical mold with a 5 cm diameter and height under conditions of optimal humidity (10-12%). The hardening occurred under a condition of almost 98% humidity.

The substantial differences in the chemical compositions of the slag under study (Table 1) are the result of significant differences in metallurgical processes and the requirements of the end metal produced. The greatest difference involves the blast furnace and converter slag compositions, especially insofar as the amounts of SiO_2, CaO, Al_2O_3, MnO, FeO +Fe_2O_3, and SO_3 are concerned. Open hearth and electric steel slag compositions are more similar (except in terms of the quantity of Al_2O_3 and FeO +Fe_2O_3) and are situated between the first two slags.

Table 1. Chemical compositions of the ferrous metallurgy slags under study.

Types of slag	Chemical composition, weight %										
	SiO_2	MgO	CaO	Al_2O_3	MnO	FeO + Fe_2O_3	S com	TiO_2	L.d.c	Σ	M_a
Blast Furnace	35.2	3.5	36.1	10.6	2.0	4.0	3.7	0.9	0.9	100.6	0.69
Open Heart	17.5	18.1	26.7	6.1	2.0	22.1	0.2	0.8	6.8	100.0	1.85
Electric Steel	18.4	16.5	29.6	10.9	4.2	16.2	0.5	0.7	0.5	99.1	1.57
Converter	19.5	1.75	56.1	2.14	6.7	11.0	0.1	0.5	0.7	99.96	2.67

Where: modulus of alkalinity $M_a = \dfrac{CaO + MgO}{SiO_2 + Al_2O_3}$

L.d.c. – Losses during calcinations.

The differences in the chemical compositions of all types of slag lead to distinct values of modulus alkalinity, M_a, which is one of the most important indicators of the binding properties of inorganic materials. Converter slag has the best M_a while blast furnace slag has the worst.

4 RESULTS AND DISCUSSION

4.1 Mechanical Properties

Converter slag shows the fastest and most constant increase in strength in hydrated slag samples (Figure 1, curve 4), which reach 40 MPa at one year of age. This is to be expected in view of this slag's chemical composition, i.e., large amounts of CaO – 56.1 % and of Mg – 1.8 % and relatively small quantities of SiO_2 – 19.5 % and Al_2O_3 – 2.1 %, which result in an M_a value of 2.67. Electric steel slag shows the best strength on the 28th day (3.9 MPa), but the worst (16.2 MPa) in the 6th year. Blast furnace and open-hearth steel slag show very competitive strengths in every stage, but display practically the same strength by the end of the 6th year, i.e., close to 20 MPa.

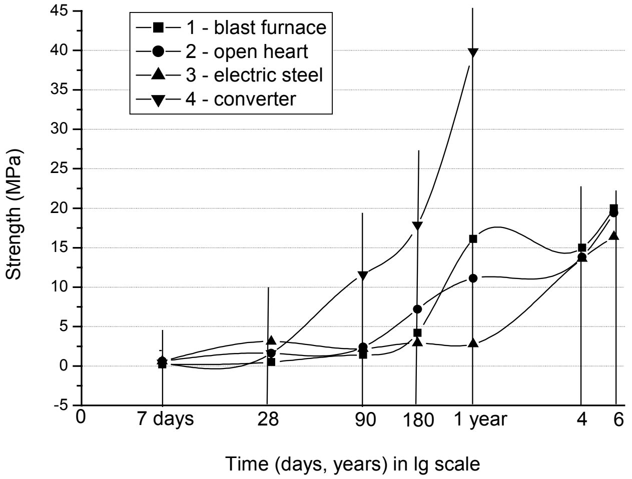


Figure 1. Strengthening of hydrated DFS from different metallurgical processes: 1 – Blast Furnace, 2 – Open Hearth, 3 – Electric Steel, 4 – Converter.

The water and frost resistance of all the types of DFS under study are given in Table 2.

Table 2. Water and frost resistance coefficients of ferrous slags.

Slag	Rw	Cw	Cf
Blast furnace	0.39	0.28	0
Open hearth	2.69	1.15	0.96
Electric steel	2.60	1.21	0.48
Converter	12.22	1.06	0.74

where: $C_w = \frac{Rw}{Ra}$ and $C_f = \frac{Rf}{Rw}$,

C_w and C_f - water and frost resistance coefficients of samples,

R_w - strength of 90-day-old samples kept under air-humid conditions (94-96% of humidity) after 24 h saturation in water,

R_a – strength of 90-day-old samples kept under air-humid conditions (94-96% of humidity),

R_f - strength of water saturated sample after 25 cycles of freezing and thawing (-25^{0}C and +20^{0}C in water), each cycle lasting 16 hours.

Russian standard requirements for road base materials from natural soils strengthened with industrial wastes after 90 days of hydration are 6-4 MPa, 4-2 MPa, 2-1 MPa, which correspond to road classes I, II and III. The lowest permissible coefficient of frost-resistance, C_f, of these materials is, respectively, 0.75, 0.70 and 0.65. This means that the strength of water-saturated converter slag, R_w, is far greater (more than double) than the standard's highest requirements. The R_w of open hearth and electric steel slag conforms to class II of the standard, but the frost resistance coefficient, C_f, of the latter falls short of the standard's requirements. Its low water and frost resistance values preclude the use of blast furnace slag without special activation of its binding properties. We have achieved excellent results in terms of activation, to be presented in our next paper.

The results listed in Table 2 confirm our conclusions, based on the values of modulus alkalinity, M_a, in Table 1: converter slag displays the best structural mechanical properties (strength, water and frost resistance), followed by open heart, while blast furnace slag displays the poorest properties.

4.2 Physicochemical hydrated slag strengthening processes (illustrated with blast furnace slag)

The hardening processes of all these slags were studied in detail using every possible instrument, as described under the subtitle “Research Methods”. Table 3 lists the main physicochemical parameters obtained for blast furnace slag strengthening after hydration.

Table 3. Changes of the blast furnace slag strengthening indices.

Indices	Time of hardening											
	Days						Years					
	0	7	28	60	90	180	1	2	3	4	5	6
Compression resistance, MPa	-	0. 2	0.5	1.2	1.4	4.2	16.1	14.3	13.6	15.0	17.1	20.0
Coefficient of lineal deformation, %	0	0.31	0.35	0.48	2.04	1.30	1.35	1.74	2.22	2.74	3.04	1.70
ommon weight osses, (TG), %	2.75	4.24	5.13	4.87	5.59	6.18	9.39	11.1	11.0	13.0	14.0	13.5
CO_2 content, (TG), %	0.25	0.61	0.77	0.92	1.53	1.97	3.91	5.67	6.50	7.60	7.83	7.85
Bonded water losses, (TG), %	2.50	3.63	4.36	3.95	4.06	4.21	5.48	5.38	4.50	5.40	6.17	5.75
pH	8.49	9.15	9.36	9.25	9.29	9.29	9.30	8.41	8.14	8.06	8.00	7.92
Varying SiO_2 content, %	0	0.23	0.30	0.40	0.54	0.76	2.20	4.22	5.00	5.27	5.60	5.81
Varying Al_2O_3 content, %	0	0.17	0.15	0.15	0.14	0.14	0.06	0.17	0.10	0.13	0.15	0.17

Similar data were also obtained for open hearth, electric steel and converter slag, but are not given here for lack of space.

The data in Table 3 demonstrate that the compression strength of blast furnace slag increases at a slow, variable rate during the first year of hardening, reaching the value of 16.1 MPa. Over the following two years it declines, dropping to 13.6 MPa, but subsequently regains its earlier level and continues increasing until it reaches 20.0 MPa in the 6th year.

The linear deformation coefficient rises in two “waves”, peaking on the 90th day (2.04 %) and in the 5th year (3.04 %), and subsequently dropping to 1.70% in the 6th year.

The weight loss commonly occurring during heating to 1000°C consists of CO_2 content and bonded water.

The constant expansion of CO_2 involves the process by which a sample carbonizes over time. This process, which is more clearly illustrated by the DTA curves (Figure 2), is due to the constant increase of the endothermic effect over time, reaching its extreme at 850°C (Figure 2, curve 8). The carbonate peak became visible (0.77% of CO_2 upon conversion to $CaCO_3$ is equal to 1.75%) only after 28 days of the material’s hydration.

This increase was so slight for the three carbonates (calcite, magnesite and dolomite), that it was almost invisible by XRD.

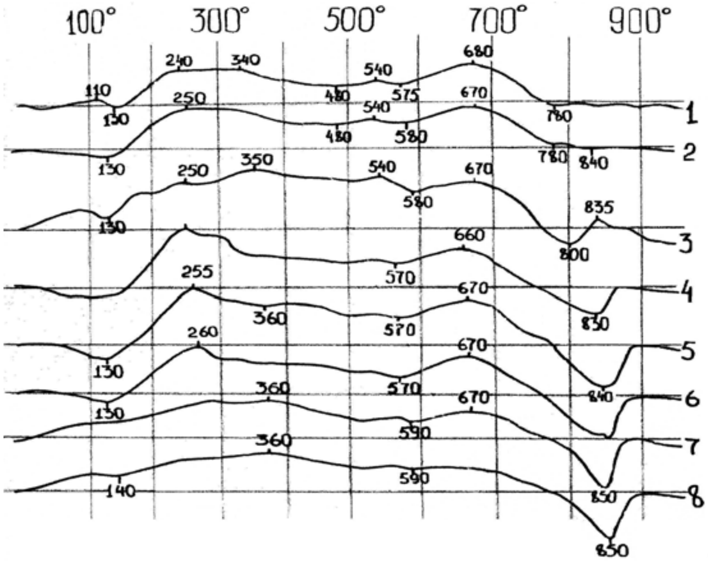


Figure 2. Changes in DTA curves during inactivated Blast Furnace Slag strengthening after hydration for 7 days (1) , 28 - (2), 90 - (3), 2 years - (4), 3 years - (5), 4 years - (6), 5 years - (7), and 6 years - (8).

At first there was endothermic maxim of 780°C resulting from the carbonates' very low level of crystalline structure formation and the presence of different types of carbonates. The increase in the quantity of carbonates and the perfection of the material's crystalline structure led to the development of the endothermic effect and caused it to shift to the right on the temperature scale, from 780°C on the 28th day to 850°C at the end of the 6th year. After the first year, the amount of CO_2 (3.91%) was only one half the amount present in the middle of the 6th year (7.85%). The material's carbonization process gradually slowed down until it almost stopped from the 4th to the 6th year.

The increase in bonded water quantity show three peaks whose maxim occurred on the 28th day and after 1 and 5 years. The loss of resistance between 1 and 4 years and the consequent increase in strength are congruent with the corresponding changes in bonded water quantity in the samples.

The pH value slowly rose from 8.49 up to 1 year (9.30), after which it dropped sharply to 8.41 (lower than initial value), after which it gradually declined to 7.92 in the 6th year.

This increase in alkalinity during first year is attributed to the process of alkaline excitement of the solid surface of slag and the removal of all the chemical elements of the slag's grains. The alkaline ions (Ca and Mg) of these elements increase the common alkalinity of pore solutions. Some of the Ca and Mg ions are bonded in very different complex compounds of new formations and are partly bonded by the CO_2 of the air present in the carbonates.

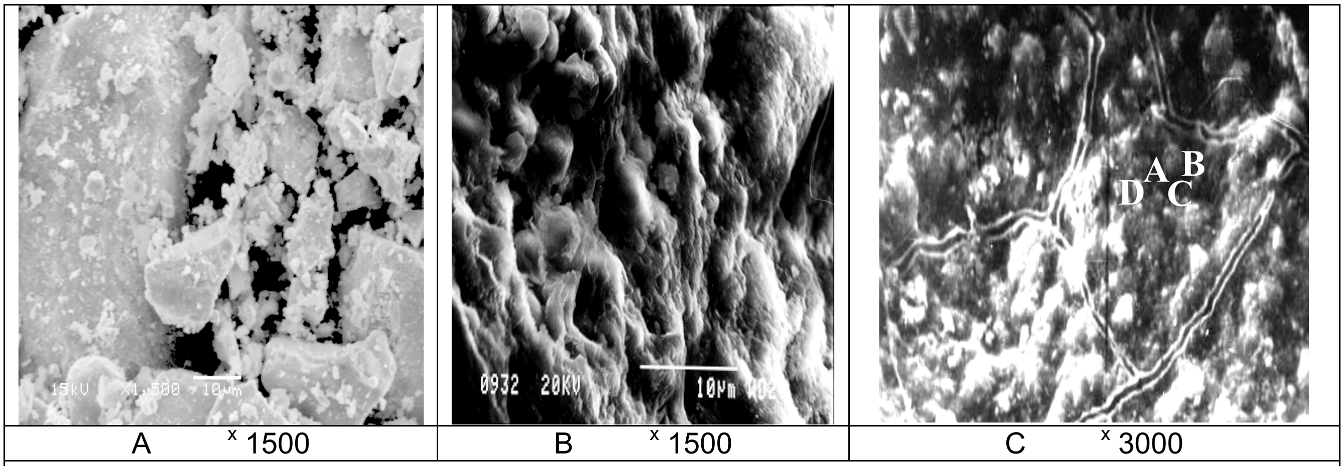
The process of leaching and removal of ions predominates during this period over the process of alkaline ion bonding and the pH increases.

At the beginning of the hydration process, the density of the pore solution is rather low, but it increases over time. Based on our observations, it appears that after the first year, the density of the new formation around the slag's solid surfaces becomes sufficiently dense to prevent future strong erosion of slag particles by alkaline pore solutions. At this point, the process of alkaline ion adsorption into the complex compounds of new formations predominates over the removal of these ions from the solid slag, and the alkalinity decreases over the second and subsequent years to levels below the original value, continuing to decrease until it reaches pH=7.92.

In our opinion, that is the main reason for the decrease in the aforementioned velocity of these materials' strengthening and carbonization.

The quite considerable density of the new formation gives rise to its process of syneresis, which is well known in colloidal chemistry. One of the main indications of syneresis is the appearance of a network of specific cracks. Such cracks are highly visible in the bodies of the slag's new formation (Figure 3 - C) at 180 days and 6 years. Due to this syneresis-related cracking, the liquid phase of alkaline pore solutions approaches the surface of solid slag particles and begins to leach out.

SEM micrographs (Figure 3) depict the transition of separate particles from the original slag (A) to the new formation over 28 days, showing rounded shapes devoid of crystal-like bodies (B). At 180 days (Figure 4-C), these rounded shapes are covered with a network of rather deep syneresis-related cracks. These cracks are subsequently sealed by the generation of fresh amorphous gel formations.



A ^{x}1500 B ^{x}1500 C ^{x}3000

Figure 3. SEM image of the Blast Furnace Slag: A – before the hydration, B – after 28 days, C – 180 days of hydration. C - Roentgen-spectral analysis points A-D of the surface of new formations (Table 4), using "Link-System".

The filling of their trenches by amorphous materials and the appearance of parapet-like shapes on both their sides evidence this crack sealing effect.

The amorphous nature of new formation is confirmed by:

1. The absence of new peaks on the XRD up to the samples' age of 6 years, with the exception of the carbonates;
2. The aforementioned absence of crystal-like shapes revealed by SEM, the presence of specific syneresis-related cracks and their sealing over time by new coatings of gel;
3. The presence of wide exothermic areas, varying from 180°C to 750°C, on the DTA curves of all ages;

4. The results (Table 4) of roentgen-spectral analysis of chemical composition on X-ray-spectral analysis (using “Link-System”) of the nearest points (A – D, Figure 3-C) of new formations of Blast Furnace Slag after 28 days of hydration were quite different;

Table 4. Chemical compositions of all most close points (typical on Figure 3-C, points A-D)

Points	Elements, %					
	Mg	Al	Si	Ca	Mn	Fe
A	5.58	23.17	18.24	51.70	0.07	1.24
B	0.77	13.28	2.43	69.81	0.81	2.90
C	1.19	16.32	47.24	34.15	0.90	0.20
D	0.10	5.77	81.24	12.43	0.02	0.44

The results of laser micro-mass analysis, similar to results of Laser micro-mass analysis by “LAMMA-1000”, Figure 4. All the spectra obtained for the chemical compositions of all the nearest points (like on the Figure 3-C) of new formations show quite dissimilar combinations of isotopes and its quantities (intensity).
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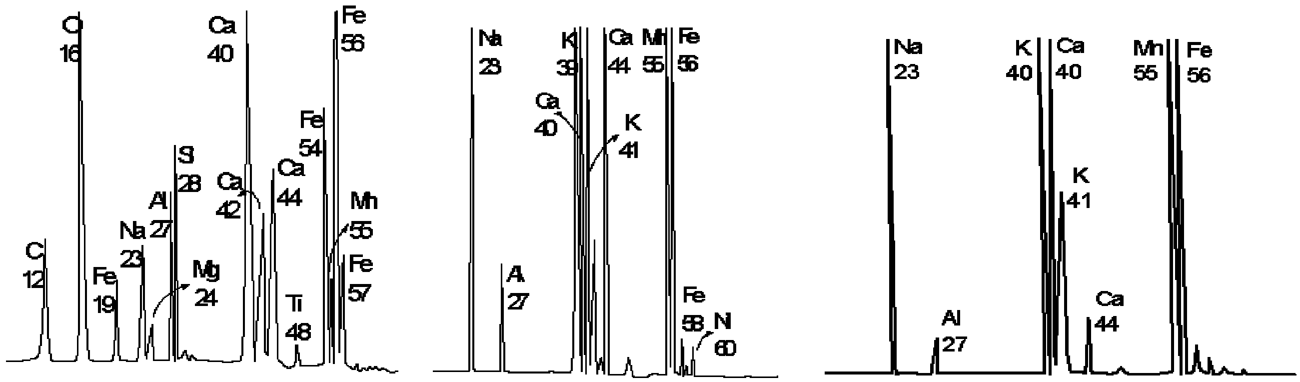

Figure 4. Typical Laser Micro-Mass Analytic (LAMMA) specters A-C of new formation (like on the Figure 3-C) on the 28th day of Blast Furnace Slag hydration.

5 APPLICATION

Some of the applications resulting from this research work were used in the construction of almost 300 km of roadbed in different parts of Russia, including the central regions of Siberia and northern Russia, which have extremely severe climatic conditions. DFS under study of various metallurgical processes were used as binder materials for the strengthening of exceedingly different natural soils as road bases. These roads with different technical categories demonstrated excellent utilization properties.

6 CONCLUSIONS

1. It was theoretically based and experimentally proved that the chemical and mineralogical compositions of some types of dumped metallurgical wastes allowed to be sure in certain binding properties of this wastes. These properties can be increased by mechanical grinding of slags and by adding of another alkaline industrial waste. They

have rather high mechanical properties (strength, water and frost resistance) and can be used as binder materials for road, airfield, dam and other base and foundation construction after their mechanical and chemical activation. These new construction materials can be used instead of sand, broken rock, gravel, sand and gravel mixes and all other traditional inert construction materials.

2. The investigations of the slag based mixtures showed that the strength of the materials increase due to the surfaces of solid particles dissolving and growth of amorphous gel compounds, their syneresis and transition to stone-like condition.

3. The developed materials and technologies are highly economically attractive because the utilization of industrial wastes for road, airfield, dum and other different base construction is 5-6 times cheaper then construction with using of traditional natural materials. So considerable decreasing of the cost is expanded by

a) the low prices of binding and activating materials (industrial wastes) reinforcing local soils,

b) the little consumption of binding material (ferrous slag) and corresponding reduction of transported materials and the transportation coast.

4. The wide-scale using of the method is environmentally effective, because the most important advantage of this method are utilizing of industrial wastes, that contaminates the environment, and reduces open-quarry extraction of natural construction materials. It is rather difficult to account the benefits of environment protection by industrial wastes utilization and its chemical binding in strong and practically dissolved combinations in acid, alkaline and neutral solutions. This fact was ascertained by two independent competent medical and sanitary expert groups.

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