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THE OBJECTIVE PREREQUISITES FOR TRANSITION TO COMPOSITE BINDERS

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Abstract.

The development of construction machinery requires urgently to create cements with new properties. To obtain high-quality concrete and improve the utilization efficiency of the cement in the concrete, the composite binders are used. The main binding component in these materials is added with special additives and active ingredients, including binding agents. This provides a substantial improvement of both the rheological properties of the cement paste and the strength and other properties of the binder and its concretes. Saving of a binding component in construction composites is one of the main tasks in the field of modern materials science in terms of saving the material resources in construction and solving major modern environmental problems of re-use of man-made materials as mineral additives in the production of construction materials.

Keywords: Composite binders, mineral supplements, active mineral additives, raw materials genesis, man-made products.

Introduction.

In the last century, concrete was on the leading place among the construction materials in the world took concrete. Nearly 15 billion m^3 of concrete is placed annually all over the world; in XX century, over 21 billion m^3 of concrete and reinforced concrete was used in Russia. Its production took more than 70% of the total cement production and

30% of non-metallic construction materials. In value terms, the concrete and reinforced concrete account for about 60% of all materials used in construction. The production performance of concrete and reinforced concrete industry to a large extent determines the level of the entire industry of construction materials. The international community has replaced the unlimited "technical progress" with the concept of sustainable development of modern civilization, which takes into account the interests of future generations. Subject to this, the construction materials and technologies should have all signs of the fifth technological wave in global development, established in the developed countries. This wave implies humanization and the greening of technologies, a high level of automation and computerization of processes, resource- and labor-saving type of reproduction, deconcentrated production, i.e. basing the concept of "sustainable construction development" on the criteria of resource- and energy-saving and environmental protection.

Almost all problems associated with negative effects of concrete on the environment, are anyhow related to its cement component. Therefore, it is extremely important from an ecological point of view to use the waste of energy, metallurgy and other industries in the production of concrete. The accumulation of waste in Russia, with all the adverse effects, is significantly ahead of their processing volumes. The cement industry is one of the main industries of construction materials, where the man-made products are used as much as possible. The waste of chemical industries such as alumino-silicate industry (ash and coal waste from heating and power plant) are widely used as raw materials. The most used material for the production of cement is the rocks from the mining and processing plants. Another known raw material components are iron ore refuses and thermophosphoric slag, but the most applicable is domain granulated slag - as an active mineral additive. Integrated use of raw materials and industrial products allows increasing the production of many kinds of products by 25-30%, reducing its cost by 2-4 times. The problem of disposal of bulk waste has international character. In the U.S. technological products utilization volume exceeds 20%, in France - 62%, Germany - 76.5%. A similar situation is in Bulgaria and Poland. Thus, further development of the technology of concrete and reinforced concrete, in the framework of "sustainable development" concept is connected with the use of composite cements, which material composition allows using fine fillers, including of man-made origin [1-5]. Due to the fact that energy consumption in the construction materials technology makes up a large part of the manufacture of cement, the cement industry is now more than ever interested in reducing fuel and electricity consumption per ton of cement produced. At the same time, the technological potential of reducing energy consumption has been almost exhausted.

The energy crisis of the 70s gave rise to the fact that scientists have started searching for new reserves for the development of the industry, adding a lot of extra components in the cement. According to the materials of the International Conference, held in Lillehammer, to achieve a further reduction in energy costs and simultaneously improve ecological safety of cement and concrete production, the European cement industry in recent years has focused on expanding the use of secondary fuels and increasing the production of composite binders (CB).

Main part.

Production of additive-containing cement already started in 1868, when the first cement factory was established in Russia. In Soviet times, annual increase in production was 25-27 million tons, and reached 140 million tons by 1990. The cement composition was changed (Table 1). In the reform period of 1991-2004, the Russian cement industry dramatically reduce the use of man-made materials - from 31 million tons in 1991 up to 16 million tons in 2004.

Table 1 - The range of cements.

Year	Cement production volume	Type of cement					Reference
		Plain portland cement (% of	Portland cement D20		Slag portland cement		
			% of total	% of mineral additives	% of total	% of mineral additives	
1950	10.2	-	-	-	-	32.4	21
1960	70.0	-	-	-	-	31.2	21
1970	95.3	63.9	34.1	24.2	27.4	30	20
1980	125.0	68.6	28	23.2	35	28.7	21
1990	84.5	71.6	28.4	20-23	23.7	22-23	21
2000	32.4	-	-	21.7	-	18.7	20
2005	48.5	91.8	80	18.0	6.1	10.6	21.23
2007	60.0	72.3	27.5	18.0	25.2	39-53	10

As a result, the proportion of clinker in the cement has increased by 11-12% and thus the share of specific material, energy and labor costs in the production of cement and its cost have also increased. The cement industry currently uses 4.5 million tons of granulated blast slag as raw materials and additives, while the resources available in the country account for about 6.5 million tons.

Nowadays, changes take place in Europe in the nomenclature of produced and consumed cement towards composite binders due to environmental and economic reasons. The development of this trend has been accelerated by the introduction of the new European standard EN 197-1, which now standardized the 27 different types of cement for general construction purposes. In accordance with EN 197-1, along with the clinker, the cement may be added with granulated blast furnace slag, pozzolans, fly ash, burnt shale and silicate dust generated in the production of a silicon and ferrosilicon alloys.

In France, production of plain portland cement was only one-quarter of the total output. The average amount of additives in 1980 amounted to 23% of French production, and now accounts for 40%. This was facilitated by the establishment of new standards, which allow adding 35% of impurities without changing the product name. Western Europe in 2005 had 44% of non-plain (impure) cements, North America in 2005 - 22%. Cement sales in Germany and the CEMBUREAU countries ("European Cement Association" (Cembureau), which unites 27 national sectoral organizations) [26], are given in Table 2.

Table 2 - The range of cements produced in Germany and CEMBUREAU countries in 2004.

Type of cement	All strength grades, %		Strength grade 32.5, %	
	Germany	CEMBUREAU	Germany	CEMBUREAU
CEM I	58	32	42	9
CEM II mixed	30	55	41	70
CEM III	11	5	16	6
CEM IV	-	5	-	12
CEM V	-	3	-	3
Others	1	-	1	-

As can be seen from Table 2, the proportion of mixed and composite binders in CEMBUREAU countries exceeds 50%, 905 of which is the share of low-grade cements. After the adoption of the new standard in the European Union, Japanese manufacturers have adopted the European experience, and brought the share of additive cement to 25%.

European approach to increase in the production of mixed and composite binders is also more acceptable because it reduces environmental pollution.

Energy consumption decreases, reducing thereby CO_2 emissions. Foreign experts believe that the era of plane portland cement has ended. Therefore, we can conclude about introduction of a new GOST 31108-2003 in the Russian Federation, which allows the very timely admixing of additives.

One of the ways of increasing the cement production is to expand the use local natural and man-made material resources (domain granulated slag, ash and slag from thermal power plants, coal beneficiation products and other materials) as raw materials and active mineral additives by increasing the production of portland cement with mineral additives, and other blended cements. In case builders increase the demand for CB and other special types of cement, while our industry together with science is capable of producing more than 80 types of cement, then the owners will stop reducing their plant capacity due to changes in the product range and other factors.

Of course, along with the construction of new and the improvement of existing facilities, the cement plants will need, in agreement with the builders, to improve the range of cement, so that they could better use its properties on their construction objects.

Therefore, now the question has aroused about binder assortment optimization, improvement of the production share of composite binders by involving natural secondary materials of various origin in the production.

Admixing the active mineral additives as an ingredient in the preparation of composite binders was a great achievement of the domestic cement industry, which has not only increased the resources of cement in the country, reduced the specific fuel consumption for its production, but also improved the durability of concrete and reinforced concrete structures. Due to the exceptional importance, CB chemistry has constituted a significant independent branch of cement chemistry.

The use of natural materials such as pozzolans, tripoli, flask, diatomite has been known since the creation of the Portland cement. With the development of metallurgical production, the cement industry obtained the opportunity to use the large amount of blast furnace slag. This contributed to rapid development of cement production as compared to metallurgical production.

In accordance with GOST 24640-91, additive components of the material composition are divided into active and mineral fillers according to their role in the process of hydration and hardening of cement. In turn, the active mineral additives by their type of activity are divided into one with hydraulic properties and with pozzolanic properties.

According to the terminology standardized by GOST 30515, “pozzolanic properties of additives" are the ability to show hydraulic properties in the presence of lime; “hydraulic properties" - the ability of fine material, mixed with water, continue to harden in water and in air after pre-hardening in air or without it.

In accordance with GOST 31108-2003, the granulated slag under GOST 3476, active mineral supplements - pozzolans (natural or man-made pozzolans, fuel ash, including acidic or basic fly ash, silica fume, gliezh and burnt schists), and an additive filler - limestone are used as mineral additives to basic components of cement, under appropriate regulatory documentation. Auxiliary cement components can be any mineral additives, which should not significantly increase the water demand of the cement or reduce the durability of concrete or protection of reinforcement against corrosion.

In the late 80-s, the RILEM Committee 73-SBC presented a classification version of man-made mineral additives (Table 3), which is made according to criteria such as the pozzolanic activity and binding properties.

This classification of man-made products allows evaluating materials in terms of their impact on the cement systems, therefore it is more objective than the usual classification of all mineral additives by their origin and role in the process of hydration.

All materials presented in the classification have a common feature - almost the same qualitative composition, but differ in the ratio of components and the degree of dispersion.

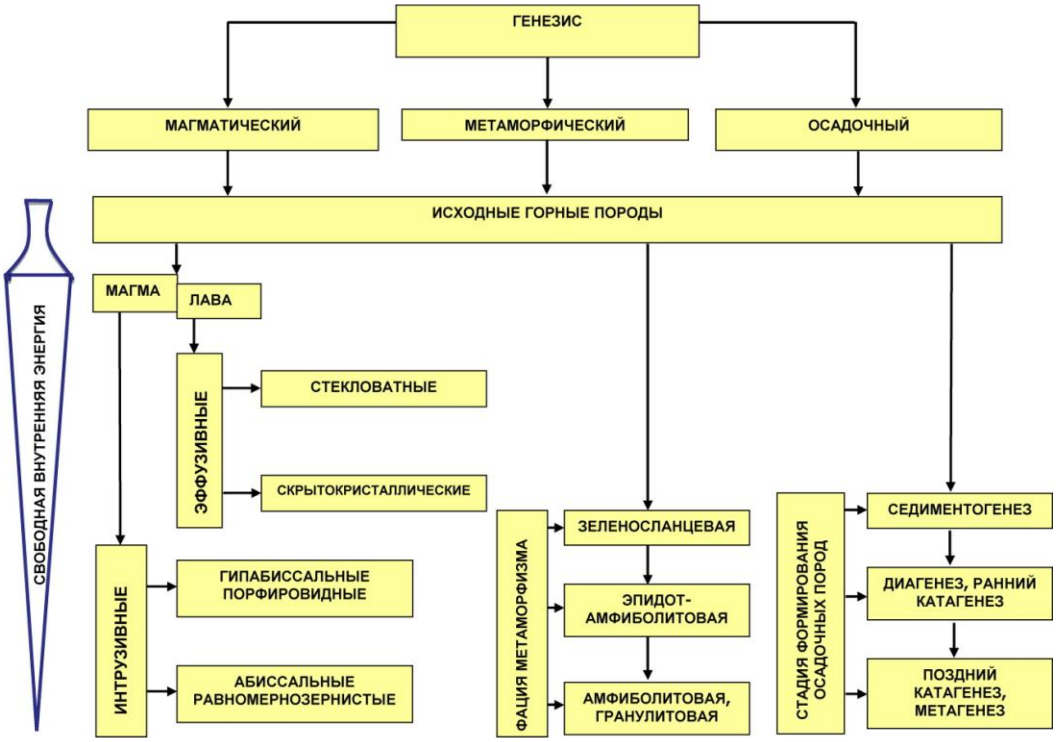
Table 3 - Classification of man-made mineral additives proposed by the RILEM 73-SBC Committee.

Classification	Chemical and mineralogical	Physical characteristics
1. With binding properties: - rapidly cooled	Mainly silicate glass (amorphous silica) containing oxides of calcium, magnesium and aluminum. May contain small amounts of crystal	Granules with 5-15% moisture content. Dried before use and ground to particles with rough surface of less than 45 microns.
2. With binding and pozzolanic properties: - high-calcium fly ash	Mainly silicate glass (amorphous silica) containing oxides of calcium, magnesium and aluminum. May contain small amounts of crystal components in the form of quartz and	Contains from 10 to 15% of particles larger than 45 μm. Most of the particles have a spherical shape with a diameter of less than 20 μm. The particle surface is
3. With high pozzolanic activity: - microsilica - rice husk ash	Consists mostly of noncrystalline (amorphous) microsilica. Consists mostly of noncrystalline (amorphous) silica.	Powder consisting of spherical particles with diameter of less than 0.5 μm. Specific surface ≈ 20,000 m^2/kg
4. With normal pozzolanic activity: - low-calcium fly ash (CaO<10%)	Mainly silicate glass (amorphous silica) containing oxides of aluminum and iron. May contain small amounts of crystal components in the form of quartz, mullite and magnesite.	Contains from 10 to 15% of particles larger than 45 μm. Most of the particles have a spherical shape with a diameter of nearly 20 μm. The specific surface - 250-350
5. Other: - slowly cooled slag - hydroremoval ash,	Contain mainly crystalline silicate minerals and a small amount of non-crystalline components.	Additionally ground to impart binding or pozzolanic properties. The ground particles have a rough

Russia has no approved unified regulatory documents for the classification of natural and man-made supplements. The rocks of sedimentary and volcanic origin, as well as some kinds of industrial waste are used as raw materials for the active mineral additives and fillers.

Technical literature distinguishes natural active mineral additives by the number of absorbed Ca^{+2} ion, based on CaO of saturated lime solution. Separately distinguished are man-made pozzolans - fired clay and shale, and ash.

In order to reduce the consumption of external energy, simplify and reduce the cost of the preparatory work, it is very expedient to search for raw materials having previously undergone geological processing that positively affected its spontaneous or artificial activation before use in construction materials technology. The work [1] shows that the value of the energy capacity of rocks and rock-forming minerals depends essentially on the genesis (Fig. 1). For example, the composition, the produced rocks, mining production waste and weathering kimberlite crust from the north diamond province of the Russian Federation differ significantly in their internal and external structure and high activity from the traditional, similar in composition raw materials used in the construction industry. It is known that conventional rocks are mined as a raw material by, as a rule, open development of the relatively small pits with a depth of 40-50 m. Meanwhile, simultaneously extracted rocks obtained after ore beneficiation are extracted from deeper deposits (450-500 m).



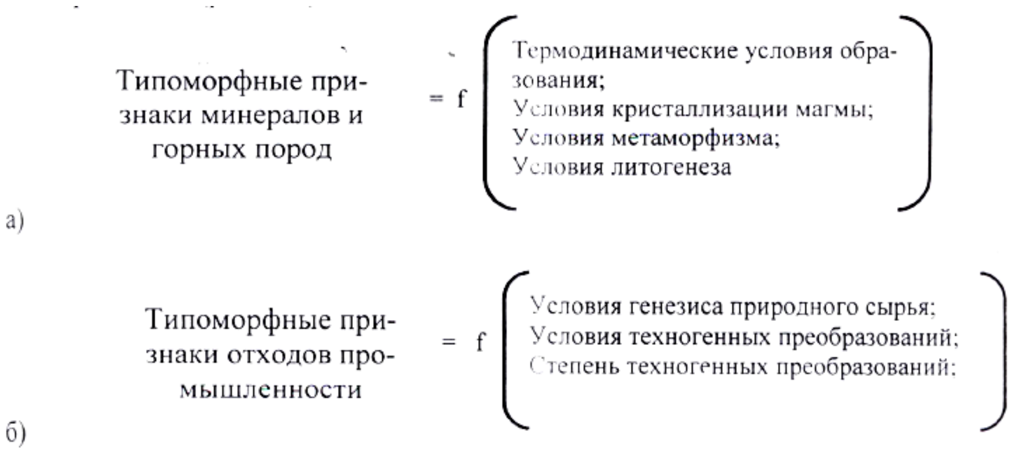
<table>
<tr><td colspan="5">Genesis</td></tr>
<tr><td colspan="3">magmatic</td><td>metamorphic</td><td>sedimentary</td></tr>
<tr><td colspan="5">Original rocks</td></tr>
<tr><td>magma</td><td colspan="4">lava</td></tr>
<tr><td></td><td>effu .</td><td colspan="3">glass-wool</td></tr>
</table>

		cryptocrystalline					
intrusive	Hypabyssal porphyric		metamorphic facies	greenshicht		Sedimentary rock formation stage	sedimentogenesis
				epidot-amphibolitic			Diagenesis, early catagenesis
	Abyssal equigrannular			Amphibolitic, granulite			Late catagenesis, metagenesis

Fig. 1. The genetic classification of rocks as a raw material for the production of construction materials

At this depth, the natural geological processes promoted technological activation of rocks as a potential raw material. This activation is usually expressed in the growth of defects in the crystal lattice of rock-forming minerals, partial amorphization of rocks and its grain structure that also undergo partial or complete destruction along with increasing specific and total surface of solid particles.

Improving the efficiency of the production of construction materials with regard to the genesis of raw materials was also studied in [2]. The author shows that the physicochemical properties of natural raw materials of construction industry - rocks and minerals, and their constituent or man-made materials - industrial waste, are a function of its typomorphic signs (Figure 2).



a)	Typomorphic signs of minerals and rocks	= f (Thermodynamic formation conditions; Magma crystallization conditions; Metamorphism conditions; Lithogenesis conditions)

b)	Typomorphic signs of industrial waste	= f (Genesis conditions of natural raw materials; Man-made transformation conditions; Man-made transformation degree)

Fig. 2. Dependence of typomorphic signs of natural raw materials (a) on industrial wastes (b) and on the genesis and technogenesis.

They, in turn, depend on the genesis of natural substances, i.e. thermodynamic conditions of their formation in the different layers of the Earth's crust, melting and crystallization conditions of magmas, subsequent conditions and the degree of metamorphism and sedimentation (Figure 2a); or on the technogenesis, i.e. the genesis of rocks, the conditions and the extent of technological transformation (Figure 2b).

Moreover, the typomorphic signs of natural raw materials in technogenesis can either dominate due to the presence of relict original forms, as happens when using mechanogenic waste; or be virtually absent, which is typical of chemogenic and pyrogenic waste. Thus, any properties of the material are determined by its genesis and typomorphic characteristics.

The author [2] argues that the information on characteristic typomorphic features of raw materials of a certain genetic type allows, without complex technology research, determining the rational spheres of use of raw materials, expanding the raw material base of the construction industry, developing the innovative production technology of construction materials, producing composite binders with predetermined properties, and reducing the energy intensity of production of construction materials.

To date, the scientists have accumulated a considerable experience in the development and implementation of composite binders representing the materials of present and future time [3-32].

Summary.

Further development of the technology of concrete and reinforced concrete, in the framework of "sustainable development" concept is connected with the use of composite cements, which material composition allows using fine fillers, including of man-made origin.

One of the ways of increasing the cement production is to expand the use local natural and man-made material resources (domain granulated slag, ash and slag from thermal power plants, coal beneficiation products and other materials) as raw materials and active mineral additives by increasing the production of portland cement with mineral additives, and other blended cements.

Therefore, now the question has aroused about binder assortment optimization, improvement of the production share of composite binders by involving natural secondary materials of various origin in the production.

In order to reduce the consumption of external energy, simplify and reduce the cost of the preparatory work, it is very expedient to search for raw materials having previously undergone geological processing that positively affected its spontaneous or artificial activation before use in construction materials technology.

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