Prospects for the utilization of solid parts of liquid waste from metallurgy for the synthesis of new materials

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Abstract

Modern metallurgic enterprises persuade ecological policy that is focused on reducing the amount of waste formation and their harmful effect on the environment. It is possible to minimize impact from metallurgical enterprises wastes on the environmental by their complete utilization.
High potential of wastes has been distinguished for their reasonable use in construction industry. It has been studied that wastes of titanium-magnesium production(industrial wastes) can be used in construction industry.

The goal of the given research is to develop the composition of building mixture for production of paving slab by using wastes from titanium-magnesium production. The experiment procedure is described and the results of carried out experiments on usage of industrial wastes from titanium-magnesium production are provided. The research resulted in development of building mixture composition with improved physical and mechanical properties on the basis of using thickened industrial wastes of titanium-magnesium production. The experiments proved that the more the content of solids in industrial wastes added to building mixtures (from 25.4 to 240.4 g/dm^3, their strength increases too depending on the time of solidification by 17.29 – 26.61 %. Optimal composition of feed stock for building mixture has been defined. This mixture can be used for production of paving slabs, manufacturing of hardscaping and for arrangement of binding course when large blocks are assembled, and also as masonry mortar for ragwork. Optimal cement:sand ratio in feed stock of building mixture is 1:3, the best water:cement ratio is 0.4, and pulp with solid residue content is 100 -240 g/dm^3.

Key words: titanium-magnesium production, industrial wastes, cement, building mortars, paving slabs

Introduction. Modern ecological standards for industrial enterprises make it necessary to create improved safe productions of processing raw material that results in conventional consumable goods, alongside with the use of technogenic wastes for the synthesis of new materials. The following problems are relevant nowadays: ecological recovery of industrial territories, utilization of technogenic wastes, purification and use of industrial wastes, sanation of polluted water and soils, reduction of gas and dust emissions into atmosphere and other. Main technogenic wastes of metallurgic enterprises are slags and slimes. Harmful effect of slime- and slag- storages of metallurgical complex enterprises is that after long period of storing, certain transformations take place that result in formation of dust, gases, chemical compounds that contaminate soil, ground and underground water and negatively affect fauna and flora. Metals and compounds concentrated in them are carried by winds, washed out by immersion type water, get into soil and carried away to water reservoirs. Concentration of such elements as mercury, stibium, zinc, lead, cadmium, sulphur, arsenic, chlorine and other elements in soils and water near industrial enterprises is usually many times more than maximum permissible concentration (MCM). Peculiarity of most wastes of metallurgic industry is that technogenic raw materials have already been processed at high temperatures, crystalline structures have been formed in wastes and don't contain organic compounds. So the author Pribulová A. et. al. (2016) shows that metallurgic slag from different metallurgic processes is treated and used in different ways depending on different characteristics of slag.

Road construction is an activity in which natural resources are utilized most of all in comparison with other branches of civil engineering. Large quantities of natural materials, break-stone, rocks and sand are built into kilometres of newly-built roads or in reconstruction of decrepit roads. At the same time, the sustainable development concept requires the more efficient management of waste materials and preservation of environment. The paper Barišić I. et. al. (2010) presents the basic characteristics of slag, describes some of foreign research studies carried out so far, and analyzes domestic experience and the possibilities of the application of slag in road building in the Republic of Croatia. Titanium-rich slag is another waste product that has emerged as an indispensable raw material for many titanium uses due to the lack of natural Tibearing resources (Peng Z. et. al. 2016). In Poland, the utilization of metallurgical waste is currently dealt with, in a majority of cases, by specialized companies. In other countries, notably in Western Europe and in the USA, ironworks treat part of their waste (e.g. slag) as a full-value product (Skuza Z. et. al. 2009). The main chemical components of these slags are silica (SiO_2), alumina (Al_2O_3), and lime (CaO), which are the main components of cement and CaO-Al_2O_3-SiO_2 (CAS) glass ceramics. Therefore, the granulated blast furnace slag (GBFS) is usually used as feedstock for cement and glass ceramics manufacturing (Zhang Y. 2019).

The most economic and effective variant of reducing metallurgic wastes is recirculation that is considerable contribution into preservation of natural resources and reduction of CO_2 emissions. As cement industry is in charge for 5-7% of world CO_2 emissions (that means 1.6 billion tons of carbon dioxide emissions going into the atmosphere), when concrete is produced , cement dosing can be reduced by using mineral additives. This strategy can also contribute into environment protection saving energy and consuming huge amount of wastes (Barbuta M. et. al. 2015). Slags characteristic, as well as their processing and use are provided in the work (Aksenova L.L., Bugaenko L.V. 2014). It has been proved that industrial slags are more reasonably used as break stone in asphaltic concrete pavements that are highly resistant to wear and possess the required fraction properties thus providing the pavement with necessary adhesion coefficient.

There is a widely used term 'technogenic deposits' in up-to-date scientific literature. Technogenic deposits are located in direct proximity to large industrial enterprises. Toxic wastes deserve particular attention among technogenic formations of metallurgic productions. It is fully applied to the wastes from production of titanium, vanadium, niobium, tantalum, and rare metal elements from ilmenite and loparite concentrates and also metal magnesium from natural carnallite. So, when spongy titanium and metal magnesium are produced from ilmenite concentrates, spent slimes, melts, radioactive dust are formed. They are industrial wastes of II-IV hazard class. They contain compounds of heavy, rare, radioactive metals (Cr, Mn, A1, Fe, Sc, Ti, V, Zr, Th, U). When metal magnesium is produced, slimes of carnallite chlorinators are formed at the final stage of carnallite melt dehydration. These slimes contain compounds of alkali metals, alkaline-earth metals and radioactive metals (Na, K, Mg, Ca, Ba, Fe, A1, Th, Ra) (Shirinkina E.S. 2009).

Conventional consumer of solid metallurgical wastes (slag, dust, clinker and other) is construction industry. Cement industry requires granulated slags, that have disordered structure of glass and consequently possessing reserves of potential energy that is evident in considerable cementing properties. Significant amount of scientific researches on secondary processing of slag wastes were carried out for recovering precious components and building material production. There are a lot of proven and implemented technologies of wastes processing on industrial scale. Wastes are processed into different building materials and applied in road construction (Kozhakhan A.K., Umbetova Sh. M. 2009).

Analysis of literature data proved that the current methods of processing wastes from titanium-magnesium production don't solve the problem of their effective neutralization. This fact calls for further exploration and development of new resource saving, environmentally-friendly technological processes for their utilization. These processes contribute to avoiding soil pollution, contamination of ground and underground waters with chlorides of different metals including highly-toxic and radioactive ones, and to rational use of mineral raw materials.

Analysis of metallurgic wastes utilization problem state in construction industry

The use of wastes as secondary material resources enables to achieve a number of important economic targets such as saving basic raw material, prevention of water, soil and air pollution, increase of details and goods production output, release of new goods for enterprises.

It has been estimated that a third of consumed raw materials resources is spent on production of manufactured goods, and two thirds is lost as by-products and wastes (Pugin KG, Vaisman Ya.I., 2013; Rusina V.V. 2007). Amount of produced wastes is particularly big when natural raw materials are processed: in mining and metallurgy industry, in chemical industry, in fuel and energy industry.

Mining and metallurgy industry is traditionally on of the basic "suppliers" of technogenic raw materials. Among metallurgical wastes, slags of ferrous and non-ferrous metallurgy are mostly used in building industry.

Characteristic feature of HPV wastes of metallurgical industry is that technogenic raw materials have already gone through high-temperature processing, crystalline structures in wastes are formed and don't contain organic compounds.

Primary consumer of slags is cement industry that annually users 20-23 mln.t of granulated product. Cooled slags are chemically active due to concealed heat energy because of glass disordered structure. Ground high-calc granulated (glass-like) slag can harden after interaction with water forming solid stone similar to cement. Hardening processes can go on at temperature 18-20^{o}C, but they are more intensive at high temperatures and in the presence of activators – lime, gypsum etc.

Steelmaking slags are used abroad for production of breakstone. In road building such breakstone is more reasonable to use in asphaltic concrete pavement. Breakstone of steelmaking slags and asphaltic concrete have high wear resistance and required frictional properties thus providing necessary adhesion coefficient to the coating.

Similarity of chemical composition of blast-furnace granulated slag with chemical composition of portland cement and glass-like state making them more chemically active predetermined the use of such slags mainly in production of portland cement and as additive to clinker and in production of slag cements.

Slag-portland cement containing 25-40% of slag is usually used in the same conditions as common portland cement. Cements containing 40-80% of slag are used as low-heat cement in massive hydraulic facilities and constructions that are subjected to the action of aggressive water as well as for production of items that undergo steam treatment.

At present different types of concrete are developed and used in building industry with the use of bonding materials, filling materials based on metallurgical slags. Cost of products made of slag concrete is 20…30% less than the cost of conventional concrete (Gaziev U.A., Akramov Kh.A. 2003).

Slags of non-ferrous metallurgy are used in small amounts yet for cement production and as ferrous component and active mineral additive, and also for production of mineral wool and cast products. Non-ferrous metallurgy slags can potentially be perspective base for production of different building materials, and their output is 1-25 times higher than output of non-ferrous metals (Tsygankov V.N. et al. 2005).

It is known that great amount of wastes are formed annually at the enterprises of titanium-magnesium production (Teplouhov A.S. 2005). Beside emerging wastes, there are more than 2 million tons of the aged wastes that have been accumulated but haven't been used. However, there is no information in the literature concerning technologic solution of titanium magnesium production wastes utilization. The exception is production of scandium from the worked out melts of titanium chlorinators and vanadium oxide from the wastes formed during purification of commercial titanium tetrachloride from impurities by the pulp of low-grade titanium chlorides (Kudryavsky Yu.P. et al. 1996).

Industrial wastes of titanium-magnesium production are characterized by variety of composition and properties and in this connection by wide range of application fields. The growth of effective functioning of titanium-magnesium production will cause the growth of wastes output. In these conditions environmentally safe titanium-magnesium production wastes utilization as secondary raw materials is becoming especially relevant, as well as development of scientific principles in creation of technologic procedures for manufacturing commercial products from wastes.

According to the previous researches it was established that main reason that restrain utilization of industrial wastes of titanium-magnesium production to its full extent is lack of consumers' conclusions about usability of chlorine-containing wastes in the production of building materials. It is connected with insufficient number of representative tests on utilization of the most chlorine-containing wastes in the production of building materials (Khairullina A.A. 2003).

Materials and methods. The object of the research is liquid wastes of titanium-magnesium production that are sent to slime storages and represent dark brown pulp with greenish shade. Chemical and phase compositions of the research object was defined with mass-spectrometer with inductively coupled plasma ICP-MS Agilent («Agilent Technologies», the USA), X-ray diffractometer PANalytical X'Pert PRO («PANalytical», the Nitherlands). In order to do this, industrial wastes were separated into solid residuals and liquid part by using centrifuge ELMI CM – 6M.01 («Elmi Ltd», Latvia). Solid residual I after triple washing with distilled water was dried at temperature 100-110 ^{o}C till its constant weight and its chemical composition was analyzed on the mass-spectrometer with inductively coupled plasma.

A mortar-mixing machine was used for preparation of building mortars. When experiments were carried out portland cement of 400-ДО grade, sand (grains size is less than 2.2 mm), water and pulp of industrial wastes of titanium-magnesium production with different solids content were used. In order to thicken industrial wastes, a laboratory thickener was used.

When building mortar of M 200 grade was produced, cement-sand ratio was 1:3 and plasticizer with water-cement ratio 0.4 was added. Industrial wastes with different content of solid residuals were charged into mortar-mixing machine together with tempering water in equal amounts.

In order to define consistency, mortar mix is put into a metal vessel with the capacity 1 litre, then it is tightened by rodding with steel core with diameter 10-12 mm (25 times) and shaked 5-6 times by slight tapping on the table. Container with mortar mix is mixed on the support so as cone nose could contact with the surface of mortar mix. The core is fastened with locking screw, and position of dial needle is fixed. Then the screw is loosened for free immersion of cone into the mortar, and after the stop second scale reading is recorded. The depth of cone immersion is defined as difference between the second and the first scale readings. Compression strength of building mortar was defined with the use of hydraulic press on three samples-cubes of 70.7x70.7x70.7 mm size aged 7-90 days. Samples strength was tested with the use of the press.

Results and discussion.

In order to study the possibility to use wastes of titanium-magnesium production when building materials and goods are produced, wastewaters of the enterprise with different solids content were used. Wastes of titanium-magnesium production were utilized and used in the manufacturing of building materials and goods. The controlled parameters were 1) for mortar mix - water holding capacity (capacity of mortar mix to hold water in its compound when it is intensively exhausted by its porous base), and 2) water requirement (water:cement ratio); for solidified mortar mix – density and strength.

A mortar-mixing machine was used for preparation of building mortars. When experiments were carried out portland cement of 400-ДО grade, sand (grains size is less than 2.2 mm), water and pulp of industrial wastes of titanium-magnesium production with different solids content were used. The strength of building mortar was researched in dependence on hardening period and solid part content in added pulp.

Table 1 provides research data concerning water holding capacity of mortar mix depending on solids content in the pulp added for preparation of building mortars.

Table 2 and Figure 1 represent dependence of mechanical strength of synthesized materials on solidification time and solids content in the added pulp. The influence of solids content in industrial wastes of titanium-magnesium production on the quality of building mortars have been researched.

Table 1 - Dependency of water holding capacity of mortar mix on solids content on the added pulp

	Solids content on the pulp , g/dm3	Water holding capacity, %
1	without adding pulp	93,0
2	25,4	93,5
3	51,6	94,0
4	103,8	92,0
5	150,3	94,5
6	240,4	92,5

Table 2 – Characteristic of researched building mortar strength

Solids content in the pulp , g/dm^3	Strength, MPa, day			
	3	7	28	90
without adding pulp	7,08	16,1	23,2	24,3
25,4	7,29	16,4	24,2	25,6
51,6	7,38	16,7	25,6	26,4
103,8	7,58	17,0	26,4	27,1
150,3	8,20	17,3	27,1	27,5
240,4	8,53	18,4	28,3	28,9

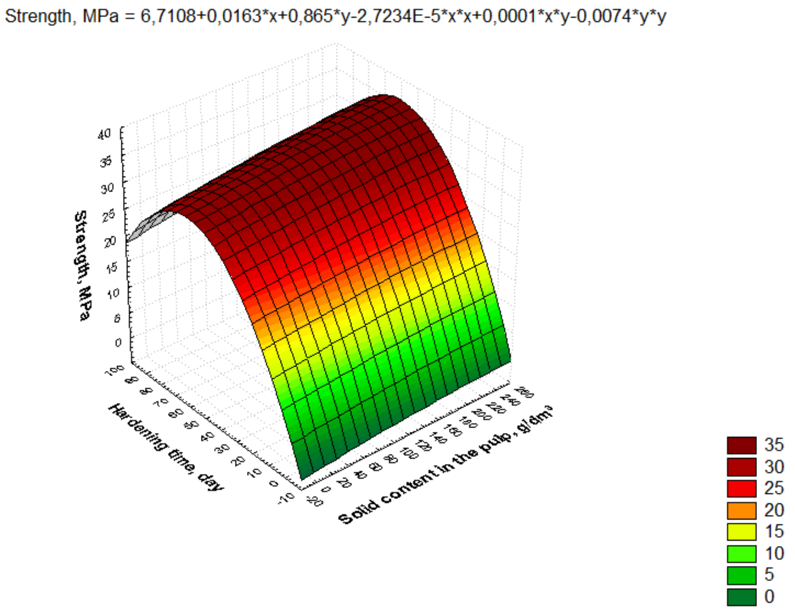

Figure 1. Dependence of mechanical strength of synthesized materials on solids content in the added pulp and solidification time

Data processing with software Statistica for Windows enabled to generate the equation for calculation of correlation matrix and graphic representation of different parameters correlation dependence.

Experimental results proved that when solids content in titanium-magnesium production industrial wastes added for preparation of building mortars, they do not influence on such factor as water-holding capacity. At the same time it was found out that when solids content is increased in industrial wastes of titanium magnesium production added for preparation of building mortars, their strength is increased too depending on the period of solidification. Thus, when amount of solids in the added pulp is increased from 25.4 до 240.4, the strength is increased by:

- 17.29 % for 3 days of solidification;
- 20.7 % for 7 days of solidification;
- 23.43 % for 28 days of solidification;
- 26.61 % for 90 days of solidification;

Thus, laboratory researches resulted in definition of optimal composition of building mixture charge that can be used for production of paving slabs, hardscaping and arrangement of underlayers when large blocks are mounted. It also can be used as masonry mortar for rag-work. Optimal cement-sand ratio in the charge of building mix is 1:3, water cement relation is 0.4, thickened pulp of industrial wastes contains 100 -240 g/dm3 of solid part.

After proportioning mortar composition, the experimental samples of paving slabs were produced with the use of optimal researched composition of building mortar. When samples of paving slabs were produced solids of industrial wastes from titanium-magnesium production were added. They were produced by the following methods:

- adding thickened pulp of industrial wastes (optimal cement-sand ratio in the charge of building mixture was 1:3, water-cement ratio was 0.4 and content of solid residual in the pulp was 150 g/dm3);
- using solid residual after centrifugation of industrial wastes (solid residual is preliminarily mixed with cement and then added to dry mix).

Figure 2 represents samples of paving slabs, that for the first time were produced with the use of solids of industrial wastes from titanium-magnesium production

Figure 2. Samples of paving slabs, that for the first time were produced with the use of solids of industrial wastes from titanium-magnesium production

Conclusions.

Thus, optimal composition of building mixture charge has been defined in the result of laboratory researches. This charge can be used for preparation of new materials with high strength characteristics for building industry. Optimal cement-sand ratio in the charge of building mix is 1:3, water cement relation is 0.4, thickened pulp of industrial wastes contains 100 -240 g/dm^3 of solid part.

From the aspect of rational nature management principle based on complete usage of primary natural resources and on bringing unused production wastes to the state when they can be assimilated by ecological systems, recovery of non-utilized industrial wastes requires further development of special technologies and technological equipment for their realization.

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