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Synthesis of New Materials Based on the Solid Phase of Liquid Titanium Metallurgy Waste

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Wastes from titanium-magnesium production are characterized by a variety of composition, properties and a wide range of applications. As a result of the research on industrial effluents utilization in titanium-magnesium production a technology was proposed that includes the separation of effluents by centrifugation into liquid and solid parts and the demineralization of the liquid part using vacuum evaporation. As a result of laboratory studies, the optimal composition of the building mixture was determined, which can be used to prepare new materials for the construction industry with high strength characteristics. Optimal cement-sand ratio in the charge of building mixture is 1:3, water-cement ratio is 0.4, thickened pulp of industrial wastes contains 100 - 240 g/dm^3 of solid part.

1. Introduction

Modern ecological standards for industrial enterprises make it necessary to develop improved safe productions of processing raw material that results in conventional consumable goods, alongside the use of technogenic wastes for new materials synthesis. 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 the atmosphere and other. Main technogenic wastes of metallurgic enterprises are slags and slimes. The 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 higher than maximum permissible concentration. Technogenic waste of metallurgical production are formed due to high temperatures exposure up to 1500 ^{o}C, so they have specific structure. The possibility of recycling industrial waste will complement the raw material base of the construction industry, reduce the cost of construction products and at the same time reduce the burden on the environment. The cement industry requires granular slag, which has a disordered glass structure and, has potential energy reserves, which is evident in significant cementing properties. A significant amount of the scientific research on slag waste recycling was carried out to restore the precious components and building materials production. There are many proven and implemented industrial waste recycling technologies. Waste is processed into various building materials and used in road construction. Pribulová et al. (2016) showed that metallurgic slag from different metallurgic processes is treated and used in different ways depending on different characteristics of slag. Utegenova et al. (2019) showed an example of the successful use of metallurgical lead and copper slags for ceramic materials synthesis for catalysis and other processes. Barišić et al. (2010) presented the basic characteristics of slag, described some of the foreign research studies carried out so far, and analyzed domestic experience and the possibilities of slag application 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 resources (Peng 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 et al., 2009). The main chemical components of these slags are silica (SiO_2),

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alumina (Al_2O_3), and lime (CaO), which are the main components of cement and CaO-Al_2O_3-SiO_2 glass-ceramics. The granulated blast furnace slag is usually used as feedstock for cement and glass ceramics manufacturing (Zhang, 2019). Zhakupova et al. (2019) suggested using technogenic waste (spent fluorohydrite) after neutralizing sulfuric acid residues as a component for the production of ceramic products for the construction industry. This will provide additional benefits from the replacement of primarily natural materials and related emissions for their search and production. The primary consumer of slags is cement industry that annually uses (20-23)×10^6 tons 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 ^oC, but they are more intensive at high temperatures and in the presence of activators – lime, gypsum etc. As cement industry is in charge for 5-7 % of world CO_2 emissions (that means 1.6•10^{12} t of carbon dioxide emissions are going into the atmosphere), when concrete is produced, cement dosing can be reduced by using mineral additives. This strategy can also contribute to environmental protection saving energy and consuming a huge amount of wastes (Barbuta et al., 2015). Aksenova et al. (2014) described characteristics of slags, as well as methods for their processing and use cases. 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, 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, Mп, Al, 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, К, Mg, Ca, Ba, Fe, Al, Th, Ra). 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. The use of wastes as secondary material resources will achieve a number of important economic targets such as saving basic raw materials, prevention of water, soil and air pollution, increase of details and goods production, release of new goods for enterprises.

2. Materials and methods

The object of the research is liquid wastes of titanium-magnesium production that are sent to slime storages and have the form of 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 Netherlands). 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 ^oC 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-DO grade, sand (grains size is less than 2.2 mm), water and pulp of titanium-magnesium production industrial wastes 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, the 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 the 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, it is then tightened by rodding with steel core with diameter 10-12 mm (25 times) and shook 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 a locking screw, and the position of dial needle is fixed. 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 a difference between the second and the first scale readings. The 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 s. Samples strength was tested with the use of the press.

3. Results and discussion

There are known cases of producing mineral fertilizers and building materials components from waste of titanium-magnesium production (Teplouhov A.S., 2005). The basic task of the works devoted to purification of industrial wastewater is providing closed water revolving (Mamutova et al., 2018). The possibility to use solid phases formed in the process of titanium magnesium production wastes purification for synthesis of new commercial products haven't been studied sufficiently (Kulenova, 2019). Slimes with different content of solids were analyzed for studying the possibility to use wastewater from the enterprise for obtaining new products. 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 the preparation of building mortars. When experiments were carried out portland cement of 400-DO 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 analyzed depending on the hardening period and solid part content in the added pulp. Table 1 provides research data concerning water holding capacity of mortar mix depending on solids content in the pulp added for the preparation of building mortars.

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

	Solids content on the pulp , g/dm^3	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

Analysis of table 1 showed that the water-holding ability of the mortar mixture in all cases remains high and ranges from 92.0 - 94.5 %. It was revealed that the solids content in the added pulp does not affect the water-holding ability of the mortar mixture. Figure 1 shows the dependence of synthesized materials mechanical strength on the solid content in the pulp and hardening time. The effect of the solid content in industrial effluents of titanium-magnesium production on the quality of mortars was investigated. As a result of laboratory studies, the optimal composition of the building mixture was determined, which can be used to prepare new materials for construction industry with high strength characteristics. It was shown that the

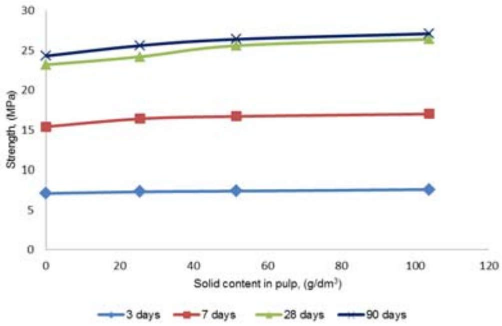

Figure 1: The dependence of synthesized materials mechanical strength on the solid content in the pulp and hardening time

mechanical strength of the samples after 3 s of extraction was 7–9 MPa at a solid phase concentration in the pulp from 0 to 250 g/dm^3. A further increase in the draw time to 7,28, and 90 d increased the mechanical strength of the test samples to 18, 26, and 28 MPa, with a maximum amount of solid phase in the pulp. At the same time, it was found out that when solids content is increased in titanium magnesium production industrial wastes added for the preparation of building mortars, their strength is increased too depending on the period of solidification. When the amount of solids in the added pulp is increased from 25.4 to 240.4, the strength is increased by: 17.29 % for 3 d of solidification; 20.7 % for 7 d of solidification; 23.43 % for 28 d of solidification;

26.61 % for 90 d of solidification. The most important indicators of the operational properties of stucco mortars prepared from dry mortars based on cement binder include:
- for mortar mixtures - mobility, water-holding ability, delamination;
- for hardened mortar - frost resistance, compressive strength, tensile strength during bending, frost resistance (for outdoor use).

To conduct the experiment on the basis of a cement binder, 7 samples of dry construction mixtures were prepared, each weighing 10 kg, with different content of solid waste from titanium - magnesium production, including a standard sample (without waste). The ratio of cement: filler = 1:1.86 (table 2).

Table 2: Composition of dry building mixtures (DBM) with the ratio of cement: filler = 1: 1.86

The composition of the DBM C,% (mass.)	The amount of waste,% by weight of filler						
	0	20	40	50	60	80	100
Cement	35.14	35.14	35.14	35.14	35.14	35.14	35.14
Sand	64.86	51.89	38.92	32.43	25.95	12.97	0.00
Waste	0	12.97	25.95	32.43	38.92	51.89	64.86

The change in the kinetics of the set of flexural strength by hardening mortars depending on the waste content in samples of dry construction mixtures on a cement binder is shown in Figure 2. It is shown that the set of

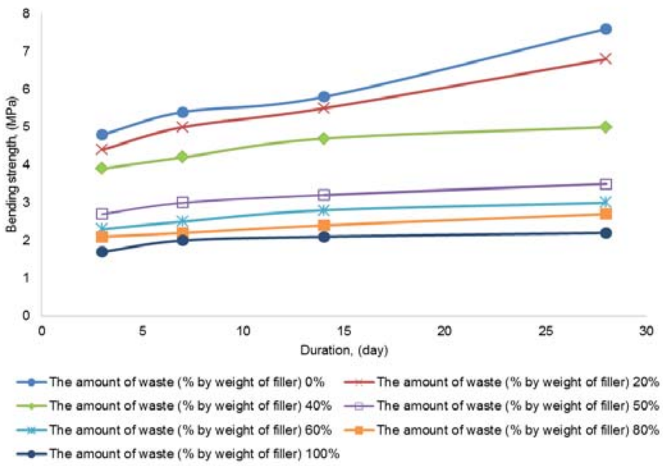

Figure 2: Kinetics of the set of flexural strength by hardening mortars, depending on the waste content in samples of dry construction mixtures on a cement binder

strength by hardening mortars occurs quite smoothly. With an increase in the exposure time of hardening mortars prepared from standard dry building mixtures (without adding waste) from 3 s to 28 s, an increase in bending strength by 37 % is observed. With an increase in the exposure time from 3 to 28 s of mortars obtained from samples of dry building mixtures with the addition of waste (from 20 to 100%), an increase in bending strength from 22 to 35 % is observed. A study of the compressive strength of these mixtures showed that without adding waste from 3 s to 28 s, an increase in compressive strength of 48 % is observed, and with the addition of waste (from 20 to 100 %) to 43 %. It was found that small addition of $CaCl_2$ (2-3 %) of cement mass promotes the decomposition of cement clinker minerals and intensifies the processes of cement hydration. Concretes with such additives, called hardening accelerators, gain strength very quickly. So, already on the third day, concrete with the addition of 2 % calcium chloride reaches 1.7 times higher strength than the concrete of the same composition, but without the addition. In the study of the solid part of the alkaline runoff, it was found that it has a high dispersion (more than 90 % with a particle content of less than 0.071 mm) and contains oxides of calcium, magnesium, iron, aluminium and calcium chloride, that proves that it is reasonable to use it as an additive in concrete mixes and mortars. The possibility of using the solid part of the industrial alkaline runoff of titanium-magnesium for the production of filling mixtures was studied. Mixed binders for filling mixtures were taken at different ratios of cement: the solid part of alkaline effluents - 70:30, 50:50, 30:70. For comparison, an inert additive (ground marl) was used as an additive with the same cement: marl ratios - 70:30, 50:50, 30:70. The introduction of the solid part of the alkaline stream into the mixture makes it possible to reduce the stratification rate of filling mixtures by 7–9 times. As the ratio of cement is increased: solid part of alkaline runoff, the strength of the bookmark increases in comparison with an inert additive (marl): 1.6 to 2.6 times with a 3-day solidification time; 1.4 - 2.5 times with a 7-day solidification time; 1.5 - 2.5 times with a 28-day solidification time; 1.37 - 2.5 times at 90 daily solidification time. It was experimentally established that the solid part of alkaline effluents of titanium-magnesium production can be used as an active additive to a binder for the preparation of filling mixtures. Along with studying the influence of mixtures composition, it was of interest to study the effect of the hardware design of the synthesis process of various building materials based on the studied waste. The effect of the centrifuge rotation speed, duration, temperature and fraction of the solid phase in the suspension on the separation of industrial waste into liquid (centrate) and solid phase (precipitate) was studied. To assess the impact of each listed factor on the degree of industrial effluents separation, a complex of studies was carried out based on the use of multi-factor experimental design technique. It was found that the centrifugation process of industrial stocks of titanium-magnesium production should be carried out for 30 minutes at a rotor speed of 3000 rpm. Replacing the existing gravitational method of utilizing industrial stocks by the method of separating suspended solids under the action of centrifugal forces will reduce the content of suspended solids 3-4 times, the solid yield is 21.85 %. The possibility of demineralization of the centrifuges obtained after centrifugation of industrial stocks from titanium-magnesium production using a rotary vacuum evaporator was studied. The condensate obtained by vacuum sublimation of industrial effluents corresponded to the technical conditions of titanium-magnesium production enterprises - industrial water for recycled water supply, mg / dm^3: chlorides - not more than 500 (in condensate 120); dry residue - not more than 2,000 (in condensate 100); suspended substances - not more than 50 (in condensate - n / a); mineralization - not more than 1000 (in condensate - 150). The solid residues obtained after vacuum demineralization contained, % (mass): 80 - 82 $CaCl_2$; 10–11 $MgCl_2$; 5-6 NaCl; 4 to 5 KCl. As a result of studies on the disposal of industrial effluents from titanium-magnesium production, a technology was proposed that includes the separation of effluents by centrifugation into liquid and solid parts and demineralization of the liquid part by vacuum evaporation. Laboratory researches resulted in the definition of the optimal composition for building mixture charge that can be used for the 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. The optimal cement-sand ratio in the charge of building mix was 1:3, water-cement relation is 0.4, the thickened pulp of industrial wastes contains 100 -240 g/dm^3 of the solid part. After selecting mixture composition, experimental samples of paving slabs were made using the optimal investigated composition of the building mixture. Samples of paving slabs were prepared by adding a solid part of industrial effluents of titanium-magnesium production by adding condensed pulp of industrial effluents (the optimum ratio in the mixture of building mix is cement: sand was 1: 3, with a water-cement ratio of 0.4 and pulp with a solid residue of 150 g/dm^3. At the next stage of the study, technological regulations were developed for designing a site for paving slabs production. Small-scale production of paving slabs, with productivity of 8-10 m^2/day was organized based on the project documentation. Paving slabs (70 m^2) were produced (35 m^2 was produced according to the developed recipe using waste, and 35 m^2 was produced without waste using standard certified technology for comparison. Technological production site and samples of experimental paving slabs are presented in Figure 3. Currently, a pilot batch of paving slab samples is being tested in practice. There is an experimental sidewalk path on the territory of D. Serikbaev EKSTU (Figure 4). In the figure, the boundary between the certified industrial slabs and the experimental pilot batch is marked in orange. The experimental track is in operation every day and is exposed to the flow of at least 2,000 students. The comparative characteristics of the initial state of the paving slab after operation for 30 s, 90 s, 180 and 365 s confirmed the high quality of the experimental batch of construction products and fullcompliance with the required technical characteristics.

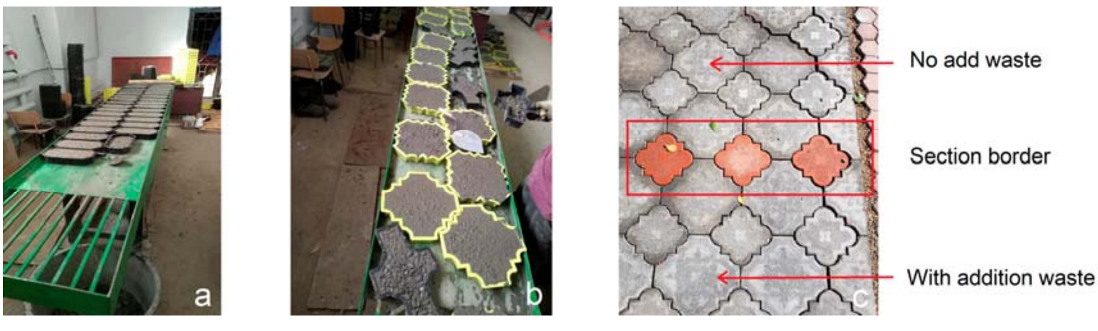

Figure 3: Prototypes of paving slabs (a) the shape of the paving slabs in the form of a "rhomb", (b) the shape of the paving slabs in the form of a "clover", (c) a fragment of the experimental track

Figure 4: An experimental track laid out of paving slabs made at the experimental site

4. Conclusions

As a result of laboratory studies, the optimal composition of the building mixture was determined for the preparation of new materials with high strength characteristics for construction industry. Experimental results showed that the solids content in industrial waste of titanium-magnesium production added for the preparation of mortars does not affect their water retention capacity. At the same time, it was found out that as the solids content is increased in industrial wastes of titanium-magnesium production that are added for the preparation of mortars, their strength increases depending on the solidification period. The optimal cement-sand ratio in the charge of building mixture is 1: 3, the water-cement ratio is 0.4, and the thickened pulp of industrial waste contains 100-240 g/dm^3 of the solid part. The optimal composition of building mixtures charge for the preparation of paving slabs was determined based on studies on the use of titanium-magnesium production wastes. Samples of paving slabs with the addition of titanium-magnesium waste was first made at D. Serikbaev EKSTU on the basis of the Test Center for Building Materials and Structures. The work outcomes contribute to waste recycling development and enable: 1) to solve the problem of titanium-magnesium production sludge collectors overfilling by decreasing the amount of the formed waste and by providing closed water revolving at an enterprise; 2) to resolve differences between economics of production and expenditures for environmental problems solving by producing commercial materials demanded by building industry.

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