N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES OF GEOLOGY AND TECHNICAL SCIENCES
ISSN 2224-5278
Volume 6, Number 420 (2016), 95 – 101

UDK 665.6/7+ 691.322 + 625.7

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HIGH POTENTIAL CONSTRUCTION MATERIALS BASED ON PETROLEUM WASTES

Abstract. This article presents the description of production processes of soil-concrete mixtures using petroleum wastes (petroleum-contaminated soils). Physicochemical and mechanical properties of petroleum-contaminated soils and soil-concrete samples have been researched. These products can be used for construction of bottom and top beds of highway and airport foundations as well as for ground stabilization.

Key words: soil-concrete, petroleum wastes, petroleum-contaminated soils (PCS), road construction.

1. Introduction. The problem of disposal of petroleum wastes accumulated as a result of activities of oil and gas enterprises has become very important these days first of all because of increased production volumes of petroleum industry. Development of effective ways of utilization will make possible conversion of hazardous wastes into valuable and safe products. It is a known fact that the drilling of oil wells leads to a severe contamination of soil and ground water with drill cuttings containing hydrocarbons, heavy metals and polymers, and that spilling of oil during production is associated with negative occurrences leading to devastation of soil and petroleum contamination of massive land areas. Oil wastes and petroleum-contaminated soils cause significant damage to environment [1, 2].

The most promising way to solve these problems is development of new technologies able to reclaim environment by using wastes to enhance quality of construction products. The wastes contain water and components that can increase the quality or partially replace expensive bitumen in asphalt concrete. Petroleum-contaminated soil may be considered as non-expensive road construction material that can be used for construction of frost blankets of roads and sidewalks as well as soil stabilizer in oil pipeline construction.

Research literature these days pays considerable attention to the issue of the use of local raw materials in production of new versions of concrete and soil-concrete. It is a known fact that cheap material leads to a cheaper end product. In our research, according to the present requirements, use of local Kazakhstani raw materials and wastes in production of soil-concrete and cement concrete is very important matter. The research utilized petroleum-contaminated soil obtained from Zhanauzen oilfields, marble cuttings from Mangistau region, different slags, brick pieces, asbestos wastes, pieces of glass and industrial wastes from Khromtau in Aktobe region[3-5].

The purpose of the research is development of technology of production of soil-concrete mixtures based on available and affordable raw materials – petroleum industry wastes, examination of physicochemical properties to define the most promising areas of their practical use.

2. Materials and Methods. Soil-concrete was prepared in the following way: petroleum-contaminated soil 30-55% by mass was mixed with Portland cement (15% by mass), sand 25% by mass, lime 5% by mass, industrial-construction wastes 30% by mass (tiles, shells, bricks, marble) in a mixer. Then water was added and the mixture was mixed to make homogenous grout.

Then mixture was poured into a mould and compacted with a metal stick or vibrator, which can be used when the mixture had a liquid or semi-liquid consistency.

Q-1000/D MOM (Budapest) derivatograph designed by F. Paulik, J. Paulik and L. Erdey was used for thermal analysis of the tested sample. The data was collected in air environment at 20-1000°C, with dynamic heating mode (dT/dt = 10 degrees/min), calibration standard sample – heat-treatedAl_2O_3,weight of the sample – 100 mg, balance sensitivity – 500 µV. Measuring sensitivity of the instrument systems: DTA = 250 µV, DTG = 500 µV, T = 500 µV.

3. Results and Discussion. We researched the composition and structure of raw material (petroleum-contaminated soil) to be used for production of soil-concrete.

Physicochemical properties of petroleum-contaminated soil obtained from Zhanauzen were determined by the way of IR spectroscopy (Figure 1). 1250 cm^{-1} shows the presence of organic-silicon compounds $Si(CH_3)_3$.

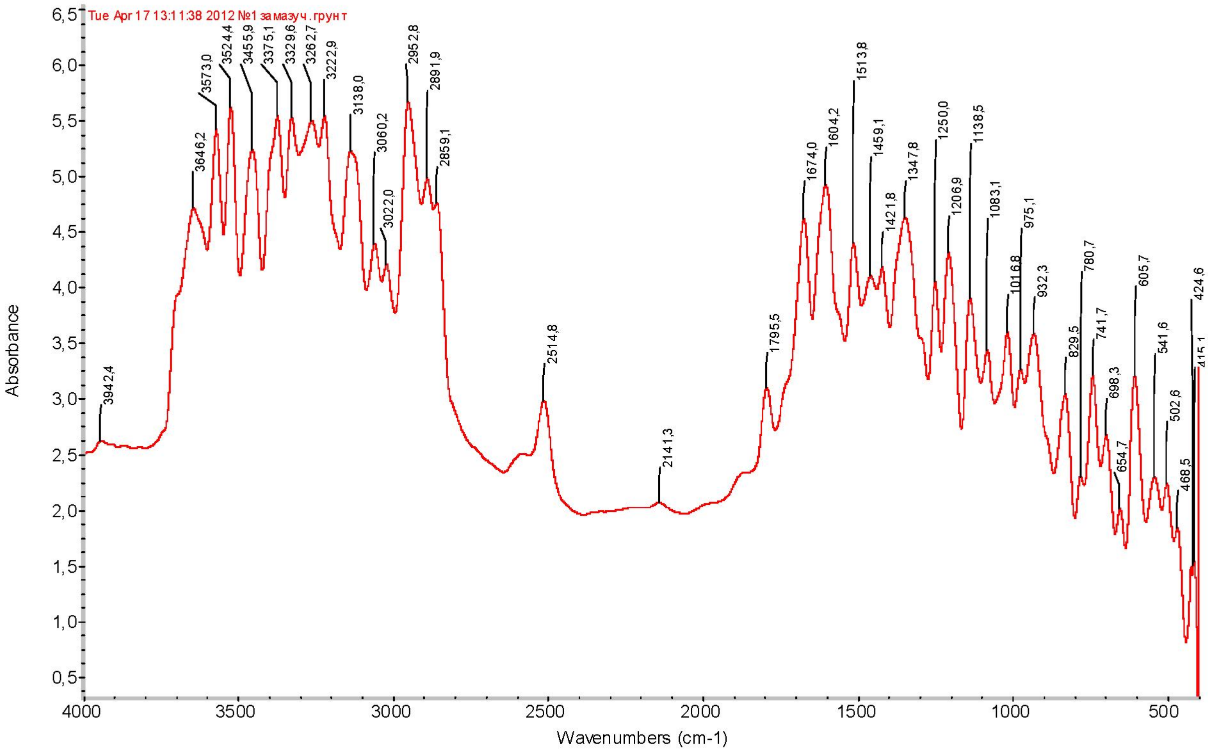

Figure 1 – IR spectrum, Zhanauzen petroleum-contaminated soil

There are also absorption bands at 2952, 2891, 2859, 1459cm^{-1}, associated with alkyl substituent's and CH_3, CH_2groups. Frequencies in the range of 3000 and3022 $cm^{-1}$are typical for rich amines and amine salts (-NH_4^+). The bands at 3646.2 3573.0 cm^{-1}, are associated with free hydroxyl groups. Absorption spectrum at 1674 $cm^{-1}$is the same for α, β–unsaturated ketones.

There is absorption band spectrum at 1083.1 cm^{-1}, typical for sulphates (asymmetric valence vibrations). At the frequency of 1604 cm^{-1}there is a presence of –COO^- carboxylates (asymmetric and symmetric valence vibrations C-O), at 1459 cm^{-1}– carbonates, at 1250 cm^{-1}– nitrites (NO_2), at 975 cm^{-1} – silicates and at 1016, 1083 cm^{-1}– phosphates and sulphates. In the range of 2859 $cm^{-1}$and 3060 cm^{-1} is typical for unsaturated alkenes and aromatic compounds (valence vibrations of methyl group). The bands in the range of 541, 605 cm^{-1},relevant to the valence vibration of C-Slink, which can point to the presence of sulfoxides and mercaptans and respective derivatives.

X-ray diffraction analysis of Zhanauzen petroleum-contaminated soil showed different minerals besides organic substances. Interpretation of X-ray diffraction analysis with the use of international reference materials showed such basic minerals as feldspars, serpentines, calcites.

Figure 2 shows that Zhanauzen petroleum-contaminated soil contains 30% of carbon atoms, 65% of oxygen atoms, mineral substance include 0.25-1.51% of magnesium, calcium, aluminum, silicon as salts and oxides.

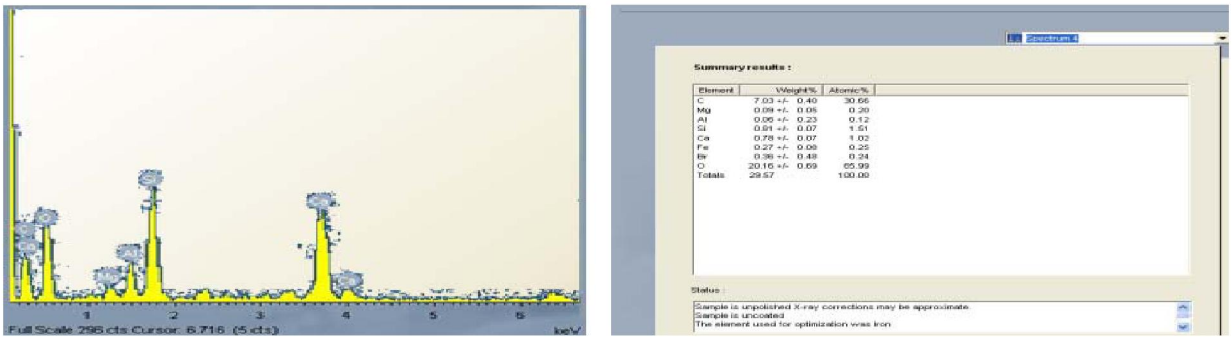

Figure 2 – X-ray diffraction analysis and chemical composition
of Zhanauzen petroleum-contaminated soil

Several samples of soil-concrete were prepared with the use of different construction wastes. Zhanauzen petroleum-contaminated soil was used along with construction wastes such as tiles, slags, bricks, shells, asbestos and glass pieces. Use of these materials in concrete production reduces the costs and helps in saving natural resources. The use and utilization of these wastes helps environmental protection.These concrete products can be used in road construction (sidewalks, highway beds) and in civil engineering.

Electron-microscopic analysis of the samples of soil-concrete was done with a scanning electron microscope (JEOL JSM – 6390 LV, JED 2300) and structural image was received at 10, 100 и 500 μm.

Figure 3 shows microstructure of the soil-concrete received with a scanning electronic microscope. It is possible to track the morphology of the soil-concrete surface using these pictures with different magnification of concrete particles.

Processing of the data defines the following:

1. Size of the particles from 20 to 400 μm
2. Particle structure – porous
3. Chemical composition, % by mass: carbon - 7.55; oxygen - 29.64; calcium-43.56; sodium - 0.33, aluminum - 2.15, magnesium - 0.70, sulphur - 2.99, silicon - 13.09 and small amount of phosphorous.

In the sample, in which the shells were used, the isolated isometric, sometimes oval pores were found (Figure 3). There are also few oval-shaped big pores (up to 40 μm) and isometric pores of “channel” type. It would seem that these pores are responsible for water adsorption.

Like all of tested soil-concrete samples, the sample with added glass pieces (Figure 4) has porous uneven structure with scarce inclusions of filler particles. Virtually ideal spherical shape of glass particles can be seen, which has a positive impact on physical and mechanical properties of composites. Glass pieces and fragments of big spheres can be also seen. Amorphous nature of glass bound by cement grout with mineral material provides strong structure resulting in better mechanical properties of soil-concrete.

In the samples with added ash and slag wastes, narrow slot-like pores as well as groups of connected irregular pores were found (Figure 5). There is also small quantity of isometric closed pores but they are relatively insignificant for the general structure porosity. Slot-like pores normally are bent, crescent-shaped but some straight pores can also be seen. Availability of small cells in the structure provides good insulating properties of concrete.

X-ray diffraction analysis of soil-concrete sample (Table 1) was done on D8 Advance (Bruker), α-Cu, 40 kv tube voltage, 40 mA current. EVA software was used for processing of diffraction patterns and calculation of planar spacing. Search/match software was used for interpretation and phase searching based on PDF-2 powder diffractometric Database. The following minerals were defined.

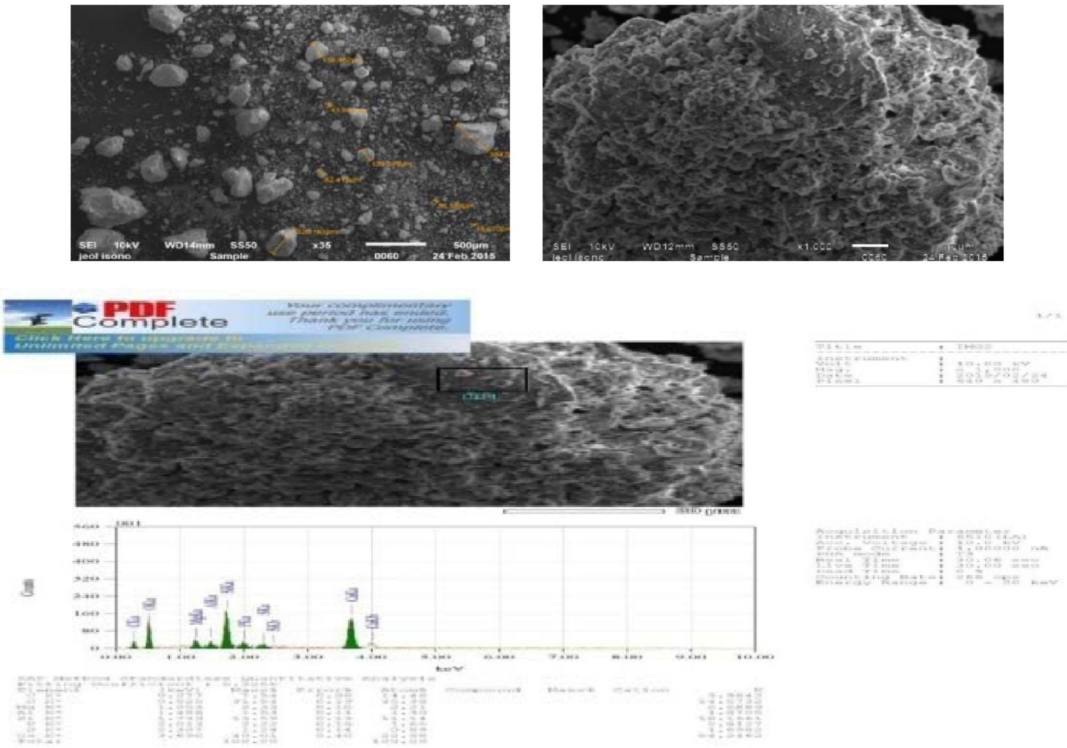

Figure 3 – Electronic image and elemental composition of soil-concrete with added shells

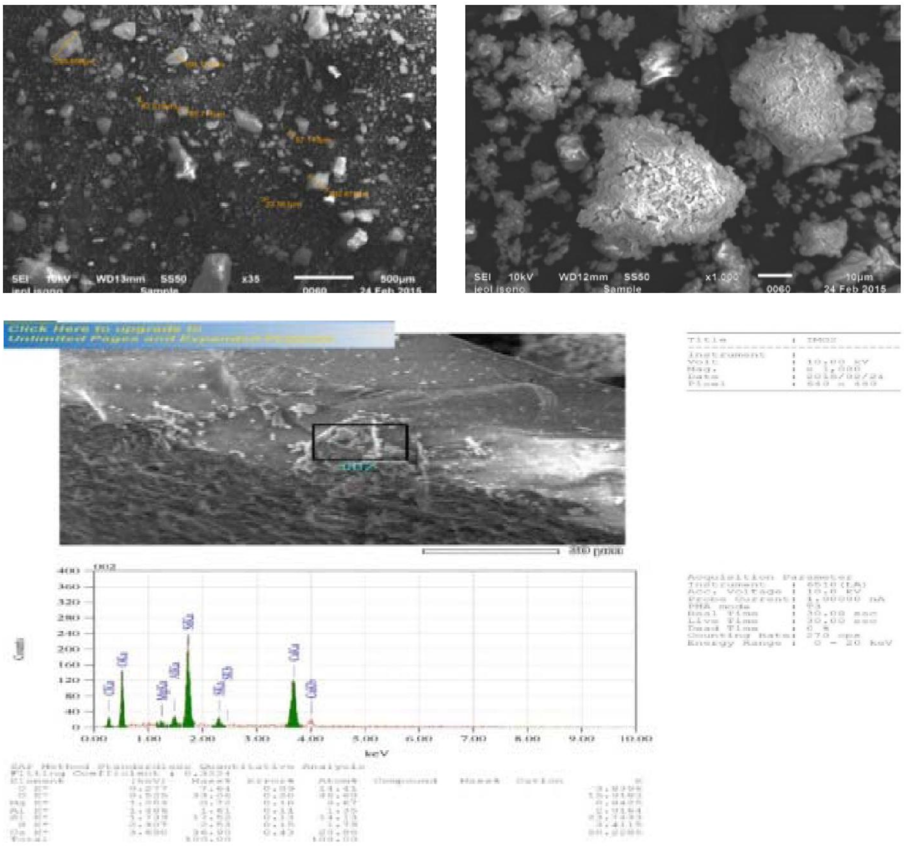

Figure 4 – Electronic image and elemental composition of soil-concrete with added glass pieces

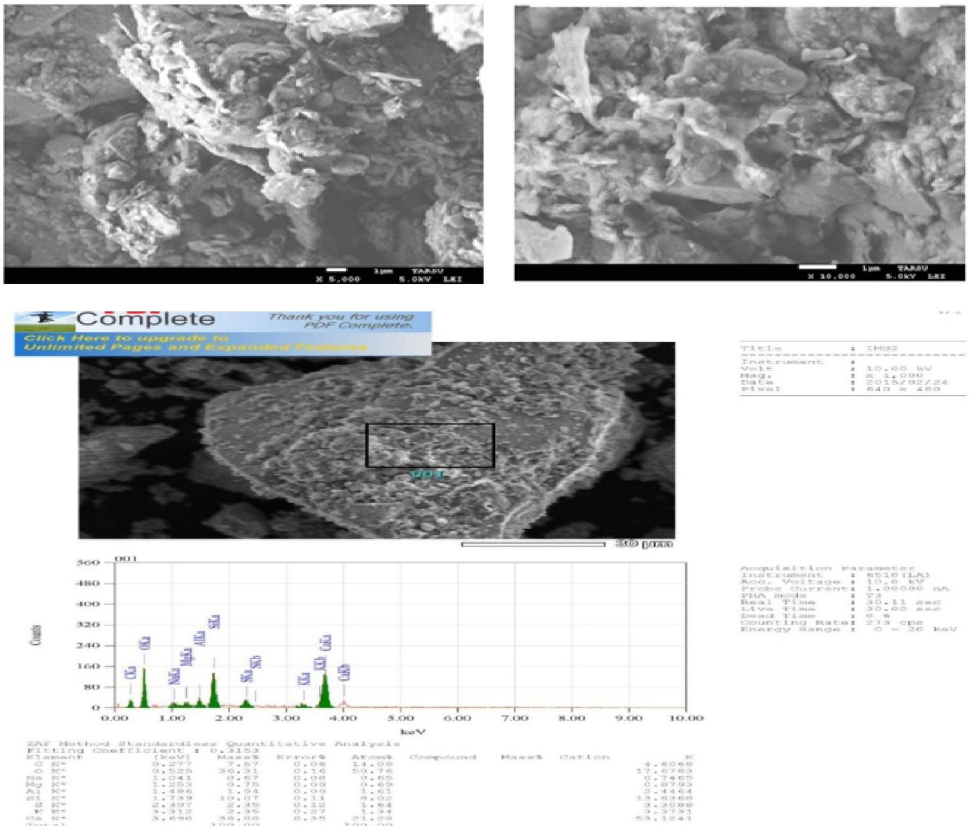

Figure 5 – Electronic image and elemental composition of soil-concrete
with added ashes and slag wastes from Almaty Heat Power Plant

Table 1 – X-ray analysis of soil-concrete with petroleum-contaminated soil

№	Compound Name	Chemical formula	S-Q
1	Calcite	$CaCO_3$	31.6
2	Microcline	$KAlSi_3O_8$	20.2
3	Quartz, syn	SiO_2	13
4	Albite, ordered	$NaAlSi_3O_8$	12.7
5	Calcium Silicate	Ca_3SiO_5	12.1
6	Anhydrite	$CaSO_4$	4.7
7	Ettringite	$Ca_6(Al(OH)_6)_2(SO_4)_3(H_2O)_{26}$	1.7
8	Portlandite, syn	$Ca(OH)_2$	1.7
9	Akermanite, magnesian, syn	$Ca_2(Mg_{0,75}Al_{0,25})(Si_{1,75}Al_{0,25}O_7)$	1.3
10	Lizardite-1M	$Mg_3(Si_2O_5(OH)_4)$	1

Differential thermal and thermal gravimetric analysis resulted in definition of sample thermal behavior and it's elemental composition (Figure 6). Thermal chemistry parameters of the tested sample showed approximate resemblance to the composition and thermal chemical properties of standard concretes.

Interpretation of differential thermal and thermal gravimetric curves of tested sample showed (directly and indirectly) presence of siliceous rocks (quartz, feldspar, potassium feldspar), carbonate minerals (as calcite (14.7%) and magnesite (<1%)with the traces of iron oxides and calcite. Several links of molecular (H_2O) and hydroxyl (OH) water were found among above formations. As well as carbon dioxide in gaseous state resulting from dissociation of $CaCO_3$.

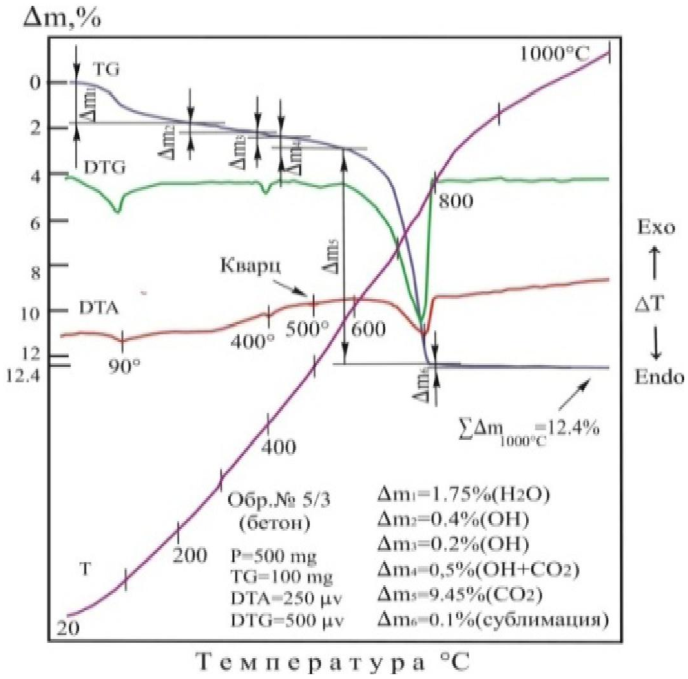

Figure 6 – Thermogram ofsoil-concrete sample

Most of molecular and hydroxyl water (~90%) was added during the mixing of soil-concrete, and only a little portion of hydrates (<10%) was the part of the components structure. The most illustrative fact proving water presence in the sample body would be prominent endothermic peaks on DTA and DTG curves found at 90 and 400°C, related to the discharge of $\Delta m_1=1.75(H_2O)$ and $\Delta m_3=0.2(OH)$ %, respectively.

Same curves in other temperature ranges donot provide adequate data on the presence of water in the system. Only thermal gravimetric curve (TG) at 220-375and 430-575°Crecorded slight weight loss associated with the change of massby$\Delta m_2=0.4(OH)$ and$\Delta m_4=1/2\cdot 0.5$ (OH) %.

The most intensive thermal reactions out of all registered during the test is the one in high temperature range. It was a result of calcium carbonate dissociation into CaO andCO_2.At the range of 675-800°C the system has the weight loss of $\Delta m_4=9.45\%$ in the form of CO_2, leaving prominent peaks on DTA and DTG curves at 780°C. In accordance with stoichiometry of $CaCO_3$and amount of lost carbon dioxide, the content of calcite in the sample is 14.7%.

There is also some (0.5%) magnesite found due to slight dip of DTG curve at 430-575°C. In this temperature range, the weight loss is 0.5%, 0.25% of which is due to CO_2.

Presence of quartz and Si, Ca, Mg, Feoxides was defined by blurred peak of polymorphic transformationα-SiO_2 into β-version and by residual principle of decomposition products.

The test date (Table 2) showed good compressive strength of water saturated samples aged for 28 days equal to 5,52-3,05 MPa, tensile bending strength of 2,25-3,05 MPa.

Table 2 – Specification of soil-concrete based onpetroleum-contaminated soil (PCS)

Composition, %									Compressive strength of water saturated samples aged for 28 days, MPa	Tensile bending strength of water saturated samples aged for 28 days, MPa
PCS	Cement	Sand	Lime	Shells	Slag	Bricks	Glass	Tiles		
55	15	25	5	–	–	–	–	–	5.52	2.65
30	15	25	–	30	–	–	–	–	7.45	3.02
30	15	25	–	–	30	–	–	–	7.43	2.98
30	15	25	–	–	–	30	–	–	6.66	2.36
30	15	25	–	–	–	–	30	–	7.12	2.25
30	15	25	–	–	–	–	–	30	7.83	3.05

4. Conclusion. Based on the above figures, one can conclude that soil-concrete mixtures have wide potential use. They can be used for bottom and top layers of highway and airport pavements, soil reinforcement during the construction of pipelines. Stabilization of industrial wastes with the help of cementing material increases opportunities of the use of soil-concrete, allowing vast stocks of widespread environment-threatening wastes to be utilized.

The work was designed by the Committee of Science of Kazakhstan.

The work was done by The Ministry of education and science of the Republic Kazakhstan project No. 1447/ГФ4 "Development of technology for dirt - asphalt mix for road construction" for the 2015–2016 year.

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СПОСОБ ПОЛУЧЕНИЯ ПЕРСПЕКТИВНЫХ БЕТОННЫХ МАТЕРИАЛОВ НА ОСНОВЕ НЕФТЯНЫХ ОТХОДОВ

Аннотация. Описаны способы получения грунтобетонной смеси из нефтяных (замазученный грунт) и строительных отходов. Изучены физико-химические и механические свойства грунтобетонных образцов. Найден оптимальный состав грунтобетонной смеси и возможность применения ее в дорожном строительстве.

Ключевые слова: грунтобетон, нефтяные отходы, замазученный грунт (ЗМ), дорожное строительство.

Работа выполнена по проекту МОН РК №1447/ГФ4 «Разработка технологии получения грунто-асфальтобетонной смеси для дорожного строительства» за 2015–2016 г.

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МҰНАЙ ҚАЛДЫҚТАРЫ НЕГІЗІНДЕГІ ПЕРСПЕКТИВТІ БЕТОНДЫ МАТЕРИАЛДАР АЛУ ӘДІСТЕРІ

Аннотация. Мақалада құрылыс және мұнай қалдықтарынан топырақбетонды қоспалар алу әдістері қарастырылды. Топырақбетонды үдгілердің физика-химилық және механикалық қасиеттері зерттелді. Топырақбетонды қоспалардың оптималды құрамы және оның жол құрылысында қолданылу мүмкіндіктері табылды.

Тірек сөздер: топырақбетон, мұнай қалдықтары, ластанған топырақ, жол құрылысы.

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