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Research of the properties of materials based on the oil wastes

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Abstract: The problem of environmental safety during handling of solid waste oil is relevant worldwide but is particularly acute in Kazakhstan almost every oil-producing region. One way of addressing arising ecological and economic problems is to briquette substandard sized coal, which will be transferred from the oil waste into the category of commercial products. Application of briquette technology of cheap coal will completely avoid the environmental benefits and also to profit from additional produced marketable products like briquettes. The paper suggested the introduction of furnace charge of the fibrous of nucleators, which are non-binding agents. By scientific studies have shown that placement of stored objects at asphalt-resinous paraffin-waste, which is a source of pollution of natural systems, it is useful material resources and can be considered as secondary raw materials. As a result of experimental research and theoretical generalizations developed resource-saving technologies that reduce the amount of accumulated solid oil waste by 30% by recycling of asphalt-resinous paraffin deposit in the preparation of waterproofing materials with desired physical and mechanical properties.

Key words: Asphalt-resinous paraffin deposit; Briquette; substandard coal; Oil; Waterproofing material; Secondary raw material

1. Introduction

In Kazakhstan the intensive development of oil and gas industry plays a leading role. The inevitable consequence of this is the growth of anthropogenic impact on the natural environment objects. In the areas of development, production, transportation, and refining of crude oil marked a violation of the natural ecological balance.

Oil and gas consumption in recent decades it has become one of the most important components of economic development of the Republic of Kazakhstan, which are in turn among the top five of ecologically unsuccessful domestic industries. In this regard, a new approach to the formulation and implementation of environmental projects of environmental protection in the oil producing region is the practical application of the tasks set by the President of Kazakhstan Development Strategy to 2030: «The environmental, sanitary-epidemiological services and standardization bodies should work in accordance with priority goals»[Nazarbayev, 1998].

Thereby, the problem of environmental safety during handling of solid waste oil is relevant worldwide, but is particularly acute in Kazakhstan almost every oil-producing region.

As studies have shown carried out by us, the treatment of oil waste should include the development of affordable and technically feasible technology for involving waste to resource management. We need new methodological approaches to solving the problem of disposal of oil waste, not traditional destructive methods and techniques to improve consumer properties, removal of unwanted impurities and components, concentration, dehydration and other enrichment methods with the use of waste in related areas of production. Such approaches of engaging waste to resource management should be the basis for the treatment of oil waste strategy and the corresponding technical solutions.

Treatment system with oil wastes should include the following steps: education, separate storage, and collection, transportation, recycling, disposal and placement in the environment non-utilizable residues. In the current practice of treatment of oil, waste is reduced to their joint collection, transportation and temporary accommodation qualitatively different waste streams, making it difficult to use further.

It can be concluded that the development of scientific and practical basis of resource-saving technologies using solid oil waste to ensure the environmental safety of natural Geosystems is an important national - economic problems for whose solution requires the development of new conceptual approaches and ecological and technical solutions.

One way of addressing arising environmental and economic problems is briquette of substandard coal

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size, which will be transferred from the oil waste into the category of commercial products. Briquetted fuel is mechanically, and a thermally robust varietal product is having a specific geometric shape, size, and weight. It is produced as a result of physical and chemical processes with the use of additives (binder) or without them. Briquettes should meet the following requirements: have a weather resistance, mechanical reliability, sufficient porosity, temperature resistance, maintain a minimum quality of water [Nazarbayev, 1998].

It was not and still doing not have in Kazakhstan, briquette factories, which are in demand among consumers. Now many private entrepreneurs are trying to set up production of briquettes, but without the scientific - technical and system training. Therefore, all attempts fail, although at first glance seems briquettes production technology is simple.

The use of coal briquette substandard technology will completely avoid the environmental benefits and also to profit from further produced marketable products - briquettes.

The paper suggested the introduction of furnace charge fibrous nucleators, non-binding. It is assumed that these nucleators will play the role of a "reinforcement," reinforcing briquettes. As known it is impossible to obtain from coal water resistant briquettes. However, the negative influence of this factor can be neutralized by treating the surface of briquettes or package them in polyethylene bags.

The calorific value of the briquettes, if not increase the ash content by the inorganic binder will be above the original coal calorific value by increasing their density as compared to the original coal.

Thus, the main parameter of optimization, in this case, is the strength of the briquettes, i.e. temporary resistance to compression (σ_c).

Based on the analysis, it was found a technological mode of briquette processing. The composition of the mixture, which includes substandard coal, the husk of rice and asphalt - resinous paraffin deposit (ARPD).

Varieties of all the complex physical - chemical and structural - rheological processes that occur during the formation of the structural frame of the briquette, due to a large number of independent factors. Therefore, the need to identify the most significant factors that have a significant influence on the intensity of adhesion, autohesion, and cohesive interactions, both during the preparation of the briquette mixture and during pressing. Results of the analysis will help to minimize the negative and maximize the positive factors in the development of the optimal composition of briquette fuel using ARPD, coal and rice husk.

Among the key factors that have a significant effect on the system structuring "ARPD - coal - rice husk" in the first place, should indicate the nature of the chemical and physical characteristics of ARPD, coal and rice husk, their ratio in the system and the condition of interaction (Fig. 1).

The dominant role in the formation of a stable frame structure owned by binding coal briquettes. Effect of binder to define a set of physical - chemical and structural - rheological properties, the main of which - the adhesive strength and cohesion depend on the chemical nature of the binder. Besides on structure formation processes have temperature, humidity, adhesive film thickness of the binder.

For briquette of culms expected to apply as binders ARPD and rice husks, which are capable of connecting fragmented solids and store them in a firm contact with significant external influences, i.e., provides a solid structure of briquettes [Nazarbayev, 1998; Ruchnikova et al., 2011].

The structure of the coal briquette can be seen as a system consisting of connecting elements and the elements at the location (dispersion medium - binders (ARPD) and the dispersed phase - coal and rice husk.)

As the result of experimental research for the production of briquettes by ASPO established process parameters briquette process. The main important factor in briquette is the establishment of quantitative and qualitative ratios of ARPD components, coal, and rice husk.

The technological scheme of briquette of coal briquettes with ARPD and rice husks have shown in Fig. 2. As shown in Fig. I of the drawing is a known system, and in II - partly based on research work proposed a new process scheme.

Small enriched concentrate 1 of size 0 - 3 mm comes to the receiving hopper (2). Further, the moving conveyor (3) passing through a 2.5 mm sieve (4), large pieces fall into the crusher (5), and to decompose 0-2,5mm. Next moving conveyor is fed into the dryer (6). In the process of drying coal is heated to 55-60º C and adjudged through the conveyor batched into a mixer (14). To avoid dust rising during handling, installed dust collectors (7).

At this time; simultaneously rice husk (8) falls into the receiving hopper (9); is dried; then through a portion of unit dose falls in the mixer (14). At that time; ARPD with special utensils heated up to 80-90ºC (11); and liquid ARPD passing through automatic measuring instrument (12) through the pipe (13) enters to the mixer (14). The mixture of solids flows into the vortex mixer for contact with the preheated at temperatures 55-60ºC ARPD. The components of briquette charge mixed and discharged into a cooling screw (15). All processes (dosage of coal and binder; loading; unloading and mixing of the charge) in a mixer (14) is automated. Briquetting mixture after cooling at screw up to 30-40 ° C flow in roller presses BVU-1 (16). Briquettes outflowing from the presses are exposed dropouts then flow into the cooling belt conveyor (17). Cooling of briquettes produced in both branches of the conveyor. To intensify the cooling process in the summer provided additional blowing air briquettes. Cooled to a temperature of 20°C briquettes conveyor transported to the point of loading. Generally in the preparation of briquettes; binders cost is 6-8% of the total weight of the briquette. When using oil waste relative costs is 9-67% (Table 1). Therefore; based on studies identified optimal mixture; where ARPD 20-25%; coal 60-75% and rice husk 5-10%.

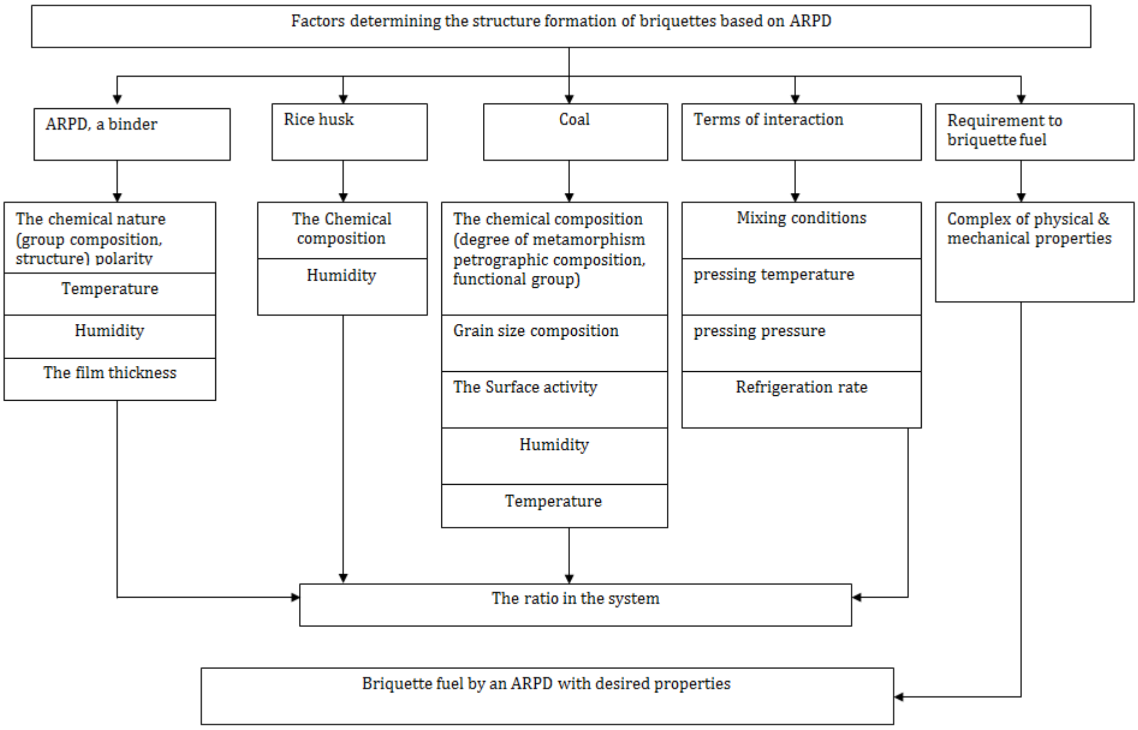

Fig. 1: An analysis of the factors determining the formation processes of briquette fuel structure by ARPD

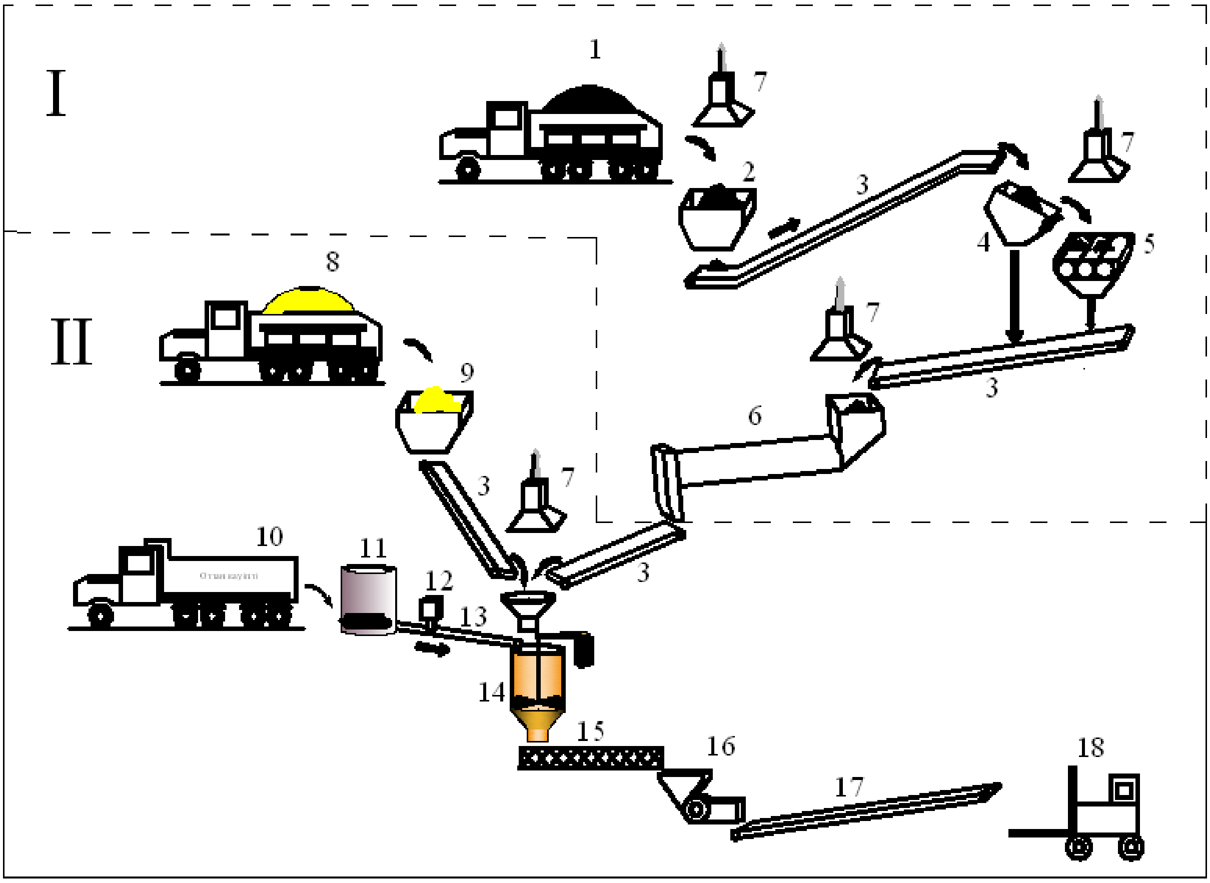

Fig. 2: Technological system of preparation briquette samples

Given the above; justified and proved the possibility of disposal of ARPD and rice husk as a binder for coal briquette. The optimal technological parameters of the briquetting process of coal waste; rice husks with ARPD. Established the optimal composition ratio of the new fuel briquette. Developed a resource-saving technology of producing a fuel based on ARPD.

Table 1: Characteristics of fuel briquette prepared on the basis ARPD

Mixture	The composition of briquette fuel; mass%		
	Briquette based on bituminous binder	Briquette-based oil waste	Briquette-based ARPD
Coal	92-94	33-91	60-75
Binder	6-8	9-67	20-25
Rice husk	-	-	5-15

Table 2: The dependence of the extraction of petroleum products from developed optimal composition of waterproofing material from the time of contact with water

The duration of contacting a sample material with water; days	The amount of extracted petroleum products per unit volume; mg/dm	pH of aqueous medium after extraction of petroleum products
1	0;16	8;32
2	0;48	8;30
3	0;55	8;27
4	0;57	8;25
5	0;58	8;23
6	0;60	8;22
7	0;60	8;20
14	0;61	8;17
21	0;70	7;15
28	0;67	7;08

The waterproofing material consisting of ASPO (19.5 ... 24.25%); clay (45 ... 50%); sand (15 ... 20%); lime (10 ... 15%); and waste tires (0.5 ... 1%); has predetermined mechanical properties: compressive strength- 85...100 kg/cm^2; water absorption- 0;7... 1;0%; filtration coefficient - 0;95·10^{-10}... 2;0-·10^{-10} m/c. Developed a new method and the appropriate technological system of preparation waterproofing material with ARPD (Fig. 2).

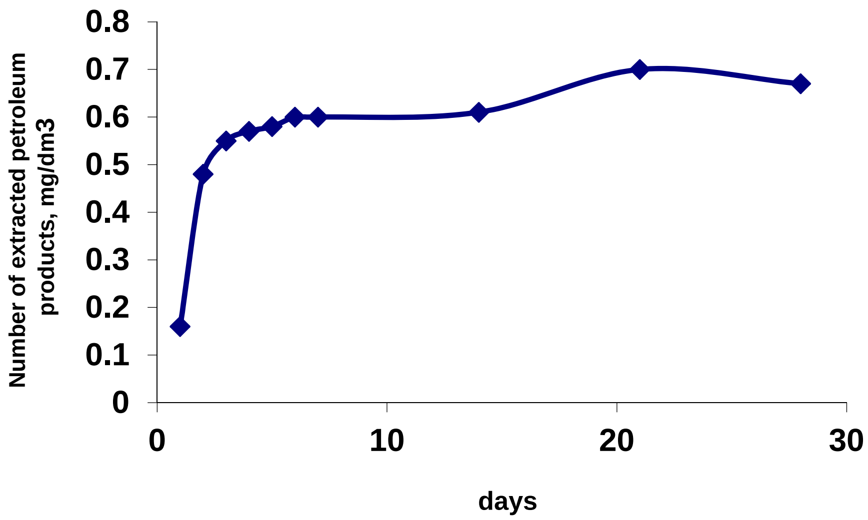

Fig. 3: The dependence of the extraction of petroleum products from developed optimal composition of waterproofing material from the time of contact with water

In the process of mechanical impact coal-ARPD-husk under the influence of temperature between the solid particles occur binder process. As a result; formed solid binded mixture. The mixture was then poured into individual shapes and pressed to a certain temperature.

While burning fuel produces heat; and the resulting heat is used in technological processes; or converted into a different energy. One of the heat producing is a carbon material.

For example; in this case; the test composition and structure of of asphalt-resinous paraffin deposits is a complex hydrocarbon compound. These oil wastes is: 80;0-86;0% carbon; 7.0-9.0% of hydrogen; 9.0% - sulfur 1;0-9;0% and 1.5% oxygen - nitrogen. also available in small amounts of resin; oil; water and mechanical impurities.

The general equation for the reaction of combustion of any hydrocarbon has the following form:

$C_m H_n + (m + n / 4) O_2 = mCO_2 + (n /2)H_2O + Q$; (1)

here m; n – the amount of carbon and hydrogen atoms in a molecule; Q-thermal effect of reaction or heat of combustion. Heat of combustion is called energy released by burning 1 kg of fuel.

In this regard is made; the mathematical model of the process of solid fuel of combustion. Presented differential equations account for all physical and chemical processes traversed by burning fuel briquettes. Given the dynamics of combustion; the method of phenomenological thermodynamics [Tanzharikov et al., 2006].

Low heat of of combustion is the most important characteristic of the fuel and for each substance is determined experimentally. When the elemental composition is known; the heat of combustion determined by the formula D.I. Mendeleev:

$Q_H^P = 339C^P + 1256H^P - 109(O^P + S_L^P) - 25.14\,(9H^P + W^P)$ (2)

here C^P; H^P; O^P; S_L^P; W^P – Fuel components: carbon; hydrogen; oxygen; sulfur; and the total value of humidity.

Based on these studies established the amount of heat of combustion of fuel briquettes under consideration. To this end; the calculations made by changing the concentration of the components in the briquette possible band reception. To calculate the compiled computer software and the results are shown in Tables 1-4 and in Fig. 1.

Based on the above stated established mathematical model for determining the heat combustion. Given all the conditions and the adopted amendments; the system of equations defining the process of solid fuel combustion obtained.

Table 3: The heat of combustion of briquettes at varying concentrations of all components

Own combustion heat			The composition of the briquette			Composition of mixture	Combustion heat Q ;kcal
ARPD	coal	Rice husk	ARPD	coal	Rice husk		
kcal / kg	kcal / kg	kcal / kg	weight part	weight part	weight part		
10400	6500	3180	0	0;9	0;1	1	**6168**
10400	6500	3180	0;05	0;8	0;15	1	**6197**
10400	6500	3180	0;1	0;7	0;2	1	**6226**
10400	6500	3180	0;15	0;6	0;25	1	**6255**
10400	6500	3180	0;2	0;5	0;3	1	**6284**
10400	6500	3180	0;25	0;4	0;35	1	**6313**
10400	6500	3180	0;3	0;3	0;4	1	**6342**
10400	6500	3180	0;35	0;2	0;45	1	**6371**
10400	6500	3180	0;4	0;1	0;5	1	**6400**
10400	6500	3180	0;45	0	0;55	1	**6429**

Table 4: The calculation results when the value is assumed constant of rice husk (10%) and the remaining concentration take different values

Own combustion heat			The composition of the briquette			Composition of mixture	Combustion heat Q ;kcal
ARPD	coal	Rice husk	ARPD	coal	Rice husk		
kcal / kg	kcal / kg	kcal / kg	combustion heat	combustion heat	combustion heat		
10400	6500	3180	0	0;9	0;1	1	**6168**
10400	6500	3180	0;05	0;85	0;1	1	**6363**
10400	6500	3180	0;1	0;8	0;1	1	**6558**
10400	6500	3180	0;15	0;75	0;1	1	**6753**
10400	6500	3180	0;2	0;7	0;1	1	**6948**
10400	6500	3180	0;25	0;65	0;1	1	**7143**
10400	6500	3180	0;3	0;6	0;1	1	**7338**
10400	6500	3180	0;35	0;55	0;1	1	**7533**
10400	6500	3180	0;4	0;5	0;1	1	**7728**
10400	6500	3180	0;45	0;45	0;1	1	**7923**

Table 5: The results of calculation to determine the heat of combustion of briquettes; constant value of coal (40%) and varying concentrations of other components

Own combustion heat			The composition of the briquette			Composition of mixture	Combustion heat Q ;kcal
ARPD	coal	Rice husk	ARPD	coal	Rice husk		
10400	6500	3180	0	0;4	0;6	1	**4508**
10400	6500	3180	0;05	0;4	0;55	1	**4869**
10400	6500	3180	0;1	0;4	0;5	1	**5230**
10400	6500	3180	0;15	0;4	0;45	1	**5591**
10400	6500	3180	0;2	0;4	0;4	1	**5952**
10400	6500	3180	0;25	0;4	0;35	1	**6313**
10400	6500	3180	0;3	0;4	0;3	1	**6674**
10400	6500	3180	0;35	0;4	0;25	1	**7035**
10400	6500	3180	0;4	0;4	0;2	1	**7396**
10400	6500	3180	0;45	0;4	0;15	1	**7757**

Table 6: The average value of the combustion heat at varying briquette concentrations of all components.

Own combustion heat			The composition of the briquette			The average combustion heat Q; kcal
ARPD	coal	Rice husk	Changes all components	Rice husk is constant	Coal is constant	
kcal / kg	kcal / kg	kcal / kg	combustion heat	combustion heat	combustion heat	
10400	6500	3180	6168	6168	4508	**5614**
10400	6500	3180	6197	6363	4869	**5809**
10400	6500	3180	6226	6558	5230	**6004**
10400	6500	3180	6255	6753	5591	**6199**
10400	6500	3180	6284	6948	5952	**6394**
10400	6500	3180	6313	7143	6313	**6589**
10400	6500	3180	6342	7338	6674	**6784**
10400	6500	3180	6371	7533	7035	**6979**
10400	6500	3180	6400	7728	7396	**7174**
10400	6500	3180	6429	7923	7757	**7369**

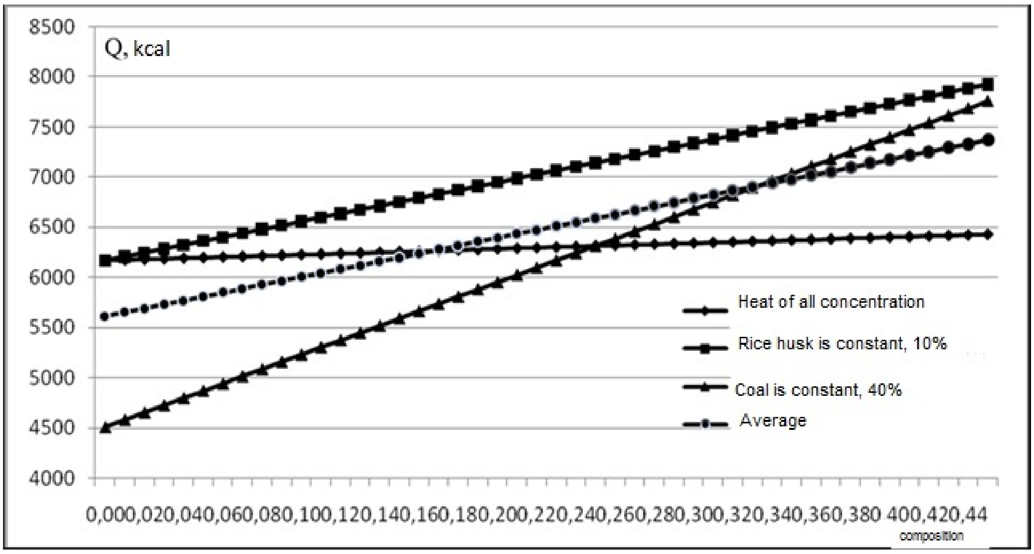

Fig. 4: The value of combustion heat of briquettes obtained for different concentrations

Integrating these equations and using approximate methods; considering only hydrogen and carbon; based on the set of simulation of mathematical models targeted average value of the heat of combustion of substances; the chemical composition of which coincides with the oil waste.

Set for fuel briquette is the minimum value of the heat of combustion is equal to Q_{min} = 4;500 kcal; and the largest value Q_{max} = 7923 kcal.

Recycling of asphalt-resinous paraffin deposits (AFS); composed of organo-mineral waterproofing compounds is based on the creation of a material with high physical and mechanical properties; using available and inexpensive components.

As has been shown; the structure of organic-mineral waterproofing material; which determines its physical and chemical characteristics; due to the properties; qualitative and quantitative indicators of the components; technological methods; conditions for the subsequent hardening.

One of the key issues to identify opportunities for the material with the desired physical and mechanical properties is the purpose of the optimal composition of organic-mineral waterproofing mixture under which it should be understood the combination of quantitative and qualitative components of ensuring compliance with the general requirements for construction waterproofing material.

To determine the optimal composition of organic-mineral waterproofing material conducted laboratory tests of samples of different composition combinations. Also; field studies have been carried out by us on an experimental site in order to justify the environmental safety and to confirm of the technical efficiency of the developed structure.

To determine the optimal composition of the material according to the results of laboratory experiments revealed samples having optimal properties using the ranking method; according to which the best is the sample for which the condition of minimum total rank properties; Rj → min. The total Rank sample properties were calculated according to the formula

$$R_j = \sum_{i=1}^{3} \lambda_i \cdot R_{ij}$$

where $\boldsymbol{R_j}$ – the total rank of sample properties; λ_i - i-th weighting factor index; which is determined by expert assessments; $\boldsymbol{R_{ij}}$ - the rank of a particular property of a particular sample.

Ranking was carried out on three independent parameters (i range from 1 to 3) defined in the course of laboratory experiments:

1) The compressive strength (σ; kg/sm); the criterial condition: σ → max; λ_1 = 0;25;

2) the water absorption (φ; in fractions %); the criterial condition: φ→min; λ_2 = 0;25;

3) the filtration coefficient (c_f; m/c); the criterial condition: c_f →min; λ_3 = 0;5;

According to the data ARPD deposits have the following average chemical composition by weight%: petroleum product (paraffin waxes; oils; resins; asphaltenes) - 80 ... 93; mechanical impurities - 1 ... 5; water - 1 ... 5.. In order to use the ARPD by the method of adsorption chromatography determined the group composition; as well as the basic properties that characterize this as a solid waste of petroleum product and the conditions of the phase transition by the methods indicated below. In experimental studies have been used ARPD selected from Akshabulak Kyzylorda region.

Characteristics:
Group compostion; weight. %:
Asphaltenes **3**
Resins 11;1
Oils:
- Paraffin-naphthenic hydrocarbons 52;3
- Light and medium aromatics **35;3**
- Heavy aromatics 5;6

Mechanical impurities 1;27
water 1;5
sulphur 0;1
The physico-mechanical and chemical properties:
Density; g/sm^3 1;0
Ring-and-ball softening point; °C 42;0
Melting temperature; °C 43-46

For the preparation of finely divided material used construction clay with a specific surface area of 15 m2 / g; building sand with a specific surface area of 25 m2 / g; hydrated lime construction; rubber; waste tires.

Extraction of petroleum products from waterproofing material carried by its contact with the water under static conditions at a temperature of 20°C. For this purpose; samples weighing 300 g was placed in a sealed container with water; the volume 3 dm and held 28 days. After 7; 14; 21 and 28 days of water samples were taken; which were analyzed for content of oil products. (Fig 3.Table 7;8)

Table 7: The values of the ranks samples properties

Indicator	Ordinal number of the sample						
	1	2	**3**	**4**	**5**	**6**	**7**
Compressive strength; Kg / cm	7	6	5	1	2	3	4
Water absorption;%	6	5	3	1	2	3	4
Filtration coefficient; $1 \cdot 10^{-10}$ m/c	7	6	1	2	3	4	5
Summary Rank sample properties	6;67	5;67	3;00	1;33	2;33	3;33	4;33

Table 8: Determination of the optimal composition range of organo-mineral waterproofing material

component mixture	Composition; mass;%			
	Sample №3	Sample №4	Sample №5	optimal composition of the mixture
Lime	15	10	15	10-15
Sand	15	20	15	15-20
Clay	43	47	45	43-47
ARPD	25	20	20	20-25
Rubber	2	3	5	2-5

The research have established the optimal mixing ratio of organo-mineral waterproofing material in mass. %: Clay - 43 ... 47; sand - 15 ... 20; lime - 10 ... 15 ... 25 -20 ARPD; Rubber - 2 ... 5.

Material of optimal composition has predetermined physical and mechanical properties: compressive strength - 85 ... 100 kg / cm2; and water absorption - 0.7 ... 1.0%; filtration coefficient - 0.95×10^{-10} ... $2\ 0 \times 10^{-10}$ m / s. Filtration coefficient at the level of regulatory requirements [1-3]; imposed to the means of protection of anti-landfills for neutralization and disposal of all types of waste.

The results showed that the sample in contact with waterproofing material from petroleum products is extracted with water. The duration of the contact with the water samples (one; two; three or four weeks) did not significantly affect the content of petroleum products in water samples (0;60-0;70 mg/dm^3). This indicates that the extraction process is much faster. Increasing the contact time does not affect the extraction of petroleum products from the material. This positive factor may be used in the operation screen with a waterproofing material is developed.

To determine the optimal composition of the proposed organic-mineral waterproofing material conducted laboratory tests of physical and mechanical properties of samples of different composition combinations. Mass content of components in the material samples was varied%: ARPD - 9 ... 25; Clay - 40 ... 60; sand - 10 ... 25; lime - 5 ... 20 ... 5 -1 tires; with step varying the amount of each ingredient in the mixture is 5% or less. The composition of the material samples and the results of laboratory studies of their properties are given in Table 9.

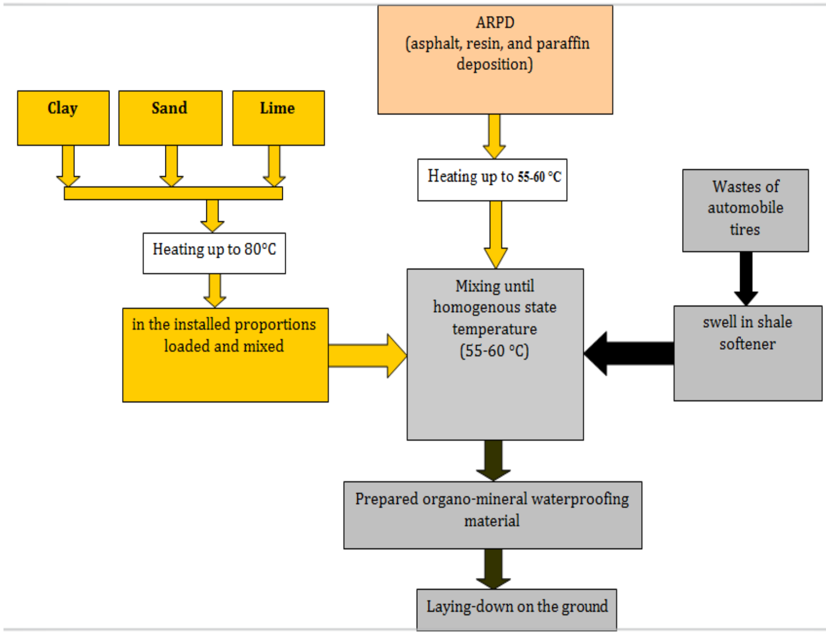

Fig. 4: Technological scheme of the sample preparation of organo-mineral waterproofing material on the basis of ARPD

Table 9: Results of laboratory tests of samples of the proposed organic-waterproofing material of different composition

№	Indicators	Composition;mass. %						
		Lime-20 Sand-10 Clay-60 ARPD-9 Rubber-1	Lime-5 Sand-25 Clay-40 ARPD-25 Rubber-5	Lime -15 Sand -15 Clay -43 ARPD -25 Rubber -2	Lime -10 Sand -20 Clay -47 ARPD -20 Rubber -3	Lime -15 Sand -15 Clay -45 ARPD -20 Rubber -5	Lime -12 Sand -17 Clay -46 ARPD -22 Rubber -3	Lime -12 Sand -15 Clay -43 ARPD -25 Rubber -5
		1	2	3	4	5	6	7
1	Compressive strength; Kg / cm	37	40	85	120	100	95	88
2	Water absorption;%	1;35	1;1	0;96	0;65	0;70	0;90	0;95
3	Filtration coefficient; $1{\cdot}10^{-10}$ m/c	5;50	4;40	0;90	1;44	1;55	2;00	1;60

The scientific significance of the work is to expand opportunities to increase waterproofing material production using oil waste as a secondary raw material stock, in order to solve environmental problems of oil producing regions of the Kyzylorda region.

Developed in the laboratory waterproofing material that meets the regulatory requirements, it proves to be true pilot tests and pilot projects.

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