Research of the composition of cement-sandy binders modified by waste of processing of petroleum bituminous rocks

T K Kuatbayeva*1, Z M Zhambakina1, G S Abiyeva2, and G O Karshyga2
1T.Basenov Institute of Architecture and Construction, Satbayev University, Almaty, Kazakhstan
2KSU named after Korkyt ATA, Kyzylorda, Kazakhstan

E-mail: aitzhanova.tokzhan@mail.ru

Abstract. The paper deals with the issues of technology of binding silicate materials with the use of mineral waste from the processing of petroleum bituminous rocks (PBR) – optimization of the ratio of raw components of the mixture of binders, development of optimal technological parameters for their production. The optimal compositions of binders were studied using waste from the processing of PBR as an activating component of cement. The influence of mechanic and chemical activation on the change in the acid-base parameters of the suspension from the crushed material was revealed. The effect of the content of additives on the degree of hydration was studied. The influence of the hardening conditions on the strength of the binder with additives of waste from the processing of PBR was studied. As a result of the experimental work carried out, technological processes for the production of binders based on waste from the processing of PBR were justified and developed. The optimal ratio of the mixture of waste from the processing of PBR with cement and the technological parameters that allow ensuring the optimal grade of the cement-sand binder are found. Silicate materials based on it have high physical and mechanical properties, meet regulatory requirements and have high resistance under operating conditions.

1. Introduction
Cements make up the leading nomenclature of the entire range of building materials and products. The creation of new binding systems and technologies for the synthesis of artificial stone, the development of energy-saving silicate and composite construction materials, determines the need to develop the basics of hydration synthesis of silicate and aluminosilicate construction materials, allows creating and developing local material production with full self-sufficiency of resources, including measures for waste disposal, reducing the energy and material intensity of product production [1].

In Kazakhstan, the reserves of petroleum bituminous rocks (PBR) amount to about 20 billion tons. Their specific composition determines the need for their integrated industrial development [2]. Due to the lack of data on the use of PBR and mineral products of their processing for the production of silicate materials of various densities, it became necessary to develop scientifically based technologies for the production of binders of construction materials using the polymineral component of PBR, the technology of silicate materials based on them.
Technogenic waste from the processing of PBR is a carrier of a significant amount of free energy, which implies that this energy is used to the maximum extent, reducing energy costs to a minimum at various technological stages [3].

The use of dispersed PBR processing products with an amorphous unstable structure makes it possible to intensify the technological process, accelerate the synthesis (hardening) of the material and reduce fuel and energy costs due to their increased reactivity. The hardening of highly dispersed systems containing amorphous and unstable phases and having excessive surface energy proceeds through a contact-condensation mechanism, with the formation of structures with phase contacts, which allows for directional control of structure formation in materials that harden without heat treatment [4].

Silicate materials based on waste from the processing of PBR are characterized by high quality indicators, have high performance characteristics and are recommended for replacing traditional cement [5].

2. Materials and methods

The following raw materials were studied: natural PBR (Kulzhan field, Atyrau region); mineral part of the processing of this rock; sand of the Embinsky field; sand of the Makat field; sand of the Nikolaevsky field; Portland cement of the Shymkent cement plant.

The determination of the material composition of raw materials and manufactured materials, their phase and structural transformations was carried out on the basis of research results, using methods of physical and chemical analysis [6].

Studies were conducted on the synthesis of silicate materials by waste from the processing of PBR - as an activating component of the cement-sand binder.

The physical and mechanical properties of the cement-sand binder were determined on solutions with the ratio: mixed binder (cement with additives) with sand - 1:1.25 (binder: sand) by weight at W/C=0.30. The number of materials per batch: binder - 170 g, sand - 425 g, water - 53 g.

The activity of cements with mineral additives was evaluated by the specific surface area and their mineralogical composition. The optimal compositions of cement-sand binders were selected depending on the hardening conditions: when hardening under normal conditions – cement clinker 70%, PBR sand 30%, compressive strength 46.0 MPa, the beginning of setting 1 h 50 min; when hardening in an autoclave – cement clinker 50%, PBR sand 50%, compressive strength 53.8 MPa, the beginning of setting 2 h 20 min.

3. Results and discussion

The approach based on contact-condensation structure formation, which allows reducing technological energy consumption due to the free energy of interacting components, is taken as a basis for the selection of raw materials [7].

Chemical, physical and mechanical, mineralogical and structural features of PBR and mineral products of their processing (Tables 1-2; Fig.1) are represented by dispersed systems of amorphous or submicrocrystalline structure, characterized by a significant reserve of free kinetic energy [8].

| Raw materials | SiO<sub>2</sub> | Al<sub>2</sub>O<sub>3</sub>+TiO<sub>2</sub> | Fe<sub>2</sub>O<sub>3</sub> | CaO | MgO | K<sub>2</sub>O | Na<sub>2</sub>O | SO<sub>3</sub> | p.o.i. |
|---------------|---------------|----------------|----------------|-----|-----|-----------|-----------|-------|-------|
| Natural PBR   | 71.6          | 8.2            | 1.8            | 1.1 | 0.12| 1.5       | 0.84      | 0.48  | 15.1  |
| PBR waste     | 82.6          | 9.3            | 2.0            | 1.3 | 0.3 | 1.8       | 1.2       | 0.8   | 1.4   |
| Portland cement of Shymkent cement plant | 23.0          | 8.8            | 4.9            | 58.4| 1.5 | -         | 0.5       | 0.6   | 1.5   |
Table 2. Physical and mechanical properties of raw materials.

| Materials                          | Average density g/cm³ | True density g/cm³ | Specific surface area, m²/kg | Fineness of grinding by the residue on the sieve N 008 |
|-----------------------------------|-----------------------|-------------------|-----------------------------|-----------------------------------------------------|
| PBR processing waste              | 1.290                 | 2.30              | -                           | -                                                   |
| Portland cement of Shemkent cement plant | 1.190                 | 3.28              | 298                         | 11.2                                                |

The possibility of using activated technogenic sands of PBR processing as additives to cement was studied.

During the grinding process, mechanic and chemical activation was applied to develop and enhance the astringent properties by jointly grinding the components of the mixture to a specific surface area of 300-1000 m²/kg (Table 3). In the process of grinding, there was an increase in the specific surface area, a change in the surface properties and structure of the grains that make up the materials. On the surface of the grains of solid crushed materials, active centers appeared, causing the hardening of mineral binders [8].

Table 3. Impact of the grinding time on the specific surface area of the PBR processing waste.

| Grinding, min | Passage through the sieve 008 mm | Grindng degree (Dₘ)% |
|---------------|----------------------------------|----------------------|
|               | PBR waste                        | Sand                 | PBR waste | Sand |
| 10            | 10                               | 6                    | 40        | 24   |
| 20            | 17                               | 10                   | 68        | 40   |
| 40            | 22                               | 20                   | 88        | 80   |
| 60            | 24.5                             | 22                   | 98        | 88   |

The activity of cements with mineral additives was evaluated by the specific surface area and their mineralogical composition (Table 3). Increased activity of sand from the processing of the PBR, after mechanical grinding, compared to the natural counterparts, is due to the partial melting of the surface of grains of the mineral rocks during thermal processing, where there is a widening crack in the cleavage of their crystals contributes to the rapid reduction, to improve the solubility and interaction with other components.

The evaluation criteria of mechanical activation were the heat of hydration of the activated mixture [9], and the strength of composite materials based on it. Depending on the type, hardness, and amount of additives, the heat of hydration varied to varying degrees. For comparison, mixtures with additives of quartz-feldspar sand, blast furnace granulated slag and without additives were considered (Table 4). It was found that the heat of hydration of the binder with additives increases, which is explained by the presence of alkalis in the waste of PBR processing [10].

Table 4. Impact of additives on the heat of hydration of the binder.

| Name of activating additives | Amount of additives % | Initial of the mixture, °C | Total amount of heat (for 3 days) cal | Heat of hydration cal/g temperature |
|-----------------------------|-----------------------|----------------------------|-------------------------------------|-----------------------------------|
| PBR waste                   | 5                     | 18,1                       | 9010                                | 53                                |
|                             | 10                    | 18,1                       | 9860                                | 58                                |
|                             | 20                    | 18,1                       | 9520                                | 56                                |
| Quartz-feldspar sand        | 5                     | 18,1                       | 8500                                | 50                                |
|                             | 10                    | 18,1                       | 9180                                | 54                                |
|                             | 20                    | 18,1                       | 9010                                | 53                                |
| Blast furnace granulated slag | 5                    | 18,1                       | 9180                                | 54                                |
|                             | 10                    | 18,1                       | 10200                               | 60                                |
|                             | 20                    | 18,1                       | 9350                                | 55                                |
| Without additives           | -                     | 18,1                       | 8840                                | 52                                |
In the process of grinding mineral additives with clinker, depending on the hardness and structure of their grinding, with the same specific surface area, their grains have different sizes. The grain surfaces of crushed PBR waste of different fractions have different pH suspensions: with the same specific surface area, the larger the fractions, the lower the pH value of the suspension, which is explained by the result of changing their surface during the grinding process. At the same time, larger fractions have an acidic character than fractions of a smaller size. Therefore, when adding waste from the processing of PBR with a smaller specific surface area, cement samples have a higher strength than finer grinding. This is due to the fact that larger fractions of the material in the suspension create a low pH value of the environment, and this contributes to the acceleration of hydration and hydrolysis of binders that have an alkaline reaction, like cement. This mechanism is based on the acid-base interaction of cement with sand products of PBR (Table 5) [11].

Table 5. Changes in the PH of the suspension of PBR processing waste.

| Name of additives         | Specific surface area, m²/kg | Fractions, mm | pH of suspension |
|--------------------------|------------------------------|---------------|-----------------|
| PBR processing waste     | 290                          | 0.5-1         | 9.4             |
| PBR processing waste     | 400                          | 1-2           | 8.4             |
| Quartz-feldspar sand     | 300                          | 2-3           | 8.0             |

The impact of the hardening conditions on the strength of the binder with additives of PBR processing waste was studied (Table 6). The samples containing 70% of cement clinker and 30% of PBR processing waste have the highest compressive strength at the age of 28 days - 46.0 MPa. After autoclave treatment, the compressive strength of samples from mixtures containing 30-50% of PBR waste is 50.0-53.8 MPa. This composition is optimal and the results obtained for compressive strength are objectively approximated with the value of the normal density, which is 27.3% and is the smallest.

Table 6. Impact of the hardening conditions on the strength of the binder with additives of PBR waste.

| Composition of mixture % | Setting time, hour-min | Normal density % | Limit of compressive strength |
|--------------------------|------------------------|------------------|-------------------------------|
| Cement clinker           | PBR waste              | beginnin ending  | in normal conditions after 28 days | at autoclaving 175°C |
| 100*                     | -                      | 1.28 3.20        | 30.2                         | 38.6 20.0               |
| 90                       | 10                     | 1.42 3.28        | 29.8                         | 42.4 43.0               |
| 85                       | 15                     | 1.40 3.20        | 28.2                         | 45.6 48.9               |
| 70                       | 30                     | 1.50 3.30        | 27.3                         | 46.0 50.0               |
| 50                       | 50                     | 2.20 3.50        | 26.3                         | 40.1 53.8               |

* - in all cases, gypsum is contained in an amount of 5% of the weight of the clinker.

Studies showed (Table 6), that the strength of the binder with additives of PBR waste depends on the hardening conditions [12]. When hardening under normal conditions, samples with a 30% sand content of PBR – 46.0 MPa, have the highest strength at the age of 28 days; after autoclave treatment, samples with a content of 30-50% of rock waste have strength of 50.0-53.8 MPa. This composition is optimal. Thus, the products of PBR processing are an active additive and increase the grade of cement.

Under the conditions of hydrothermal synthesis of the studied materials, the CaO/SiO₂ ratio changes, the basicity of calcium hydroxides decreases, the degree of polycondensation of silicon-oxygen anions increases, increasing their binding capacity. This has a positive effect on the strength characteristics of silicate materials [13].

Taking into account the physical and technical properties of cement-sand binders, the efficiency of using the developed binders in the construction industry was established.

4. Summary
Technological processes for the production of silicate materials based on technogenic mineral waste from the processing of PBR are justified and developed.
The chemical-mineralogical and structural features of mineral waste from the processing of PBR as raw materials for the production of cement-sand materials are revealed. The thermal effect of PBR processing modifies the mineral component of the rock, as a result of which the resulting sand is better ground and subjected to mechanical activation than natural sands: the duration of grinding is reduced, the degree of grinding is increased. This has a positive effect on the solubility of sand minerals and the degree of interaction with cement.

With the addition of PBR processing waste smaller specific surface of cement samples have higher strength than the more fine grinding, due to the fact that a larger fraction of material in suspension creates a low pH of environment, and this contributes to the acceleration of hydration and hydrolysis binders, having an alkaline reaction, such as cement.

Mixed binders based on cement with mineral waste from the processing of PBR have low heat and in heat-and-humidity conditions intensively gain strength, providing the required grade.

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