Research of technological properties of the composition of binding binders, modified with waste of processing of petroleum bituminous rocks

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Abstract. The paper deals with the issues of technology of grouting binders of silicate materials with the use of waste from the processing of petroleum bituminous rocks. The optimal compositions of grouting solutions with the use of waste from the processing of PBR were studied. The stability of the samples in aggressive environments of low- and high-base calcium hydrosilicates was studied. Technological processes for the production of grouting binders based on waste from the processing of PBR were justified and developed. Grouting compositions, characterized by high quality were developed. The positive effect of mixing and storage of the tested cement mixtures containing up to 50% of PBR waste with sulfate solutions of Na₂SO₄ and MgSO₄ salts on the studied technical characteristics of the grouting solution and cement stone was established. A significant result is an improvement in the setting performance, an increase in strength without a significant deterioration in the adhesion of the cement stone to the drive pipe at a 5% salt concentration. The research results provide recommendations for the development of weighted grouting cements using technogenic materials containing an increased amount of iron oxide.

1. Introduction

The development of new approaches to the creation of energy-saving and low-energy-intensive systems of silicate and composite construction materials determines the need to develop scientific and theoretical prerequisites for the physical and chemical bases of the hydration synthesis of silicate and aluminosilicate construction materials [1].

The use of dispersed PBR processing products with an amorphous unstable structure makes it possible to intensify the technological process and reduce fuel and energy costs. The hardening of highly dispersed systems with excessive surface energy proceeds with the formation of structures with phase contacts. This allows for the directional regulation of structure formation in materials that harden without heat treatment [2].

There is an objective need to conduct research to identify the mechanism of interaction of such raw materials in the process of formation of hydrate phases, structural features and their impact on the properties of composite silicate materials, for example, the durability of silicate materials, which
depends on the properties of cementitious substances and is determined by the degree of preservation of the crystallization structure in a saturated solution [3].

The behavior of silicate materials in aggressive environments also depends on the type of oxides contained in them and the amount of individual minerals. In the presence of insoluble silicates and aluminosilicates containing silica, they are acid-resistant. Rocks in which oxides corresponding to strong bases are combined with oxides corresponding to weak acids, such as calcium and magnesium carbonates, are alkali-resistant [4].

Taking into account that most of the known PBR deposits are located near oil-producing areas, where cements with special properties (grouting), in underground conditions, in contact with various mineralized waters, accompanied by high temperature conditions and pressure, are consumed in large quantities, it is necessary to conduct research on the use of PBR processing products as active additives for the production of mixed cements [5].

The use of PBR waste involves a multicomponent mixture for the production of composite materials, which is economically advantageous from an energy point of view, as the substances present in them, actively interacting, accelerate the synthesis (hardening) of the material. This makes it possible to use the potential energy of the waste more fully in creating a perfect structure of the hydrate phases with lower energy costs. The resulting materials based on PBR waste are recommended for replacing traditional grouting cements.

2. Materials and methods

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

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

During the grinding process, mechanic and chemical activation was applied to display and enhance the astringent properties by grinding jointly the components of the mixture to a specific surface area of 300 - 1000 m²/kg.

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 amount of materials per batch: binder - 170 g, sand - 425 g, water - 53 g.

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.

Taking into account the occurrence of oil deposits in the Caspian lowland in deep water, in saline environments with high temperature and pressure special experiments of mixing the test mixtures of cement content up to 50% sand products of PBR, in one case, a 5% Na₂SO₄ solution and the other with 3% solution of MgSO₄ were set. After forming, some of the samples were hardened under normal conditions, others were steamed at 75°C, and the third part was autoclaved at 175°C according to the regime (1.5+8+1.5 hours). The solidified samples were placed in solutions of sodium and magnesium sulfate. After the expiration of the storage period, they were tested for strength.

3. Results and discussion

Chemical, physical and mechanical, mineralogical and structural features of PBR and mineral products of their processing are represented by silica materials containing more than 50% SiO₂ and limestone-silica materials containing from 20 to 50% SiO₂ [7].
Table 1. Chemical composition of raw materials.

| Raw materials     | SiO₂ | Al₂O₃+TiO₂ | Fe₂O₃ | CaO  | MgO  | K₂O  | Na₂O | SO₃  | p.o.i |
|-------------------|------|------------|-------|------|------|------|------|------|-------|
| Natural PBR       | 71.6 | 8.2        | 1.8   | 1.1  | 0.12 | 1.5  | 0.84 | 1.48 | 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 Shemkent 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 |
|------------------------------------|------------------------|--------------------|----------------------------|----------------------------------|
| Waste of PBR processing            | 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. Mechanic and chemical activation was carried out, the evaluation criteria of which were the heat of hydration of the activated mixture, and the strength of composite materials based on it [8]. For comparison, mixtures with additives of quartz-feldspar sand, blast furnace granulated slag and without additives were considered [9].

Under the conditions of hydrothermal synthesis of the studied materials, the CaO/SiO₂ ratio changes, the basicity of calcium hydrosilicates decreases, the degree of polycondensation of silicon-oxygen anions increases, increasing their binding capacity, which positively affects the strength characteristics of silicate materials. When studying the composition of the cement-sand binder with sand additives from the processing of PBR, when hardening under normal conditions, the samples after autoclave treatment had the greatest strength, with a content of 30-50% of rock waste – 50.0-53.8 MPa, which indicates that PBR waste is an active additive and increases the grade of cement.

Studies were conducted on the synthesis of grouting silicate binders based on waste from the processing of PBR, to determine the resistance of the obtained cement-sand binders in aggressive environments. When studying the determination of the resistance of cement-sand binders based on waste from the processing of PBR in aggressive environments, samples made from a mixture with mixing water and hardened under steaming conditions at 75°C, after 12 months of storage in solutions of Na₂SO₄ and MgSO₄, reduced the strength by 5%, and samples made from a mixture mixing with a solution of 3% MgSO₄, hardened under the same conditions, after storage in a 5% sodium sulfate solution and after the same test periods, increased the strength by 5%, and when stored in 3% MgSO₄, increased the strength by 4%. Samples that hardened in aggressive sulfate solutions, under hydrothermal conditions, at 175°C, had absolute resistance and their strength not only did not decrease, but on the contrary increased, with the exception of samples made from a mixture mixing with a 5% solution of sodium sulfate, tested in a 3% solution of magnesium sulfate, which, after 12 months of storage, increased strength by only 2%.
The technological methods of achieving the directed phase formation necessary to increase the durability of materials (weighting of the material, increasing crack resistance), by inserting a binder, steelmaking or lead slag containing hematite and magnetite into the solution, and increasing crack resistance – by inserting specially synthesized mineral wool [10], were considered.

The strength of the investigated grouting binder with sand additives from the processing of PBR depends on the hardening conditions. The composition, quantity and types of the “salt additive” added to them, as well as the hardening conditions were chosen taking into account the conditions of the operating environment, taking into account that the mixing with sulfate solutions allowed to increase the strength of the samples in all conditions of their hardening. Moreover, with an increase in the temperature of the hardening conditions of the samples, their strength increased to a greater extent.

The results of the studies showed that the stability of samples made from a mixture mixing with water and hardened under steaming conditions at 75°C, after 12 months of storage in Na₂SO₄ and MgSO₄ solutions, reduced the strength by 5%, and samples made from a mixture mixing with a solution of 3% MgSO₄, hardened under the same conditions, after storage in 5% sodium sulfate solution and after the same test periods, increased the strength by 5%, and when stored in 3% MgSO₄, increased the strength by 4%.

Samples that have hardened in aggressive sulfate solutions, under hydrothermal conditions, at 175°C, have absolute resistance and their strength not only does not decrease, but on the contrary increases, with the exception of samples made from a mixture mixing with a 5% solution of sodium sulfate and tested in a 3% solution of magnesium sulfate, which, after 12 months of storage, increased strength by only 2%.

Mixing with sulfate solutions allowed increasing the strength of the samples in all conditions of their hardening, and with an increase in the temperature of the hardening conditions, the strength increases to a greater extent. The stability of the samples increases with the duration of storage in aggressive solutions.

### Table 3. The influence of aggressive environments on the change in the bending strength (MPa) of cements with the addition of PBR processing waste.

| Materials and conditions of preparation | Hardening conditions | Storage in Na₂SO₄ during: | Storage in MgSO₄ during: |
|----------------------------------------|---------------------|---------------------------|-------------------------|
| cement with 50% PBR processing waste and mixed with water | in normal conditions steaming at 75°C | 1 day 6 days | 12da ys |
| | autoclaving 175°C | 12da | 1da 6da | 12da |
| | | 3.6 2.7 | 1.6 3.6 2.9 | 1.1 |
| cement with 50% PBR processing waste and mixed with 5% solution of Na₂SO₄ | in normal conditions steaming at 75°C | 4.0 | 3.6 3.8 |
| | autoclaving 175°C | 4.4 4.1 | 3.3 | 4.4 4.0 3.0 |
| | | 5.2 4.6 | 4.2 | 5.2 4.8 5.0 |
| cement with 50% PBR processing waste and mixed with 2% solution of MgSO₄ | in normal conditions steaming at 75°C | 4.2 | 4.8 4.4 |
| | autoclaving 175°C | 5.8 5.5 5.8 | 5.8 | 5.9 6.0 |
| | | 6.2 6.4 6.6 | 6.2 | 6.5 6.8 |
The mechanism of insertion of sulfate salts into the composition is conventionally called the “affinity” of the cement composition with the operating environment [12]. This principle can be extended to other types of binders and aggressive environments. The positive effect of sulfate ions on the strength and sulfate resistance of binders is explained by the fact that SO\textsubscript{4} ions in the initial period of cement hydration facilitate charge transfer from the surface of the solid, and increase the surface potential, and in the late stages of hardening participate in phase formation and enter the structure of calcium hydrosilicates and hydroaluminates, changing their properties. With a significant content of SO\textsubscript{4} ions in CaO-SiO\textsubscript{2}-H\textsubscript{2}O, ellestadite is formed [13].

Taking into account that the temperature influence on the phase composition of hydrated compounds in the hardened binder adopted by the temperature setting conditions from 20 to 175\textdegree C, and pressure from 0 to 0.8 MPa (autoclaving), ensured the completeness of hydration of binders and investigated the identity of the standard binder, used in deep wells with high temperature and intraformational pressure.

Taking into account the obtained physical and technical properties of cement-sand binders (high frost resistance and corrosion resistance, availability and possibility of multi-tonnage use of the main components, reduction of costs for the production of binders, durability), the efficiency of using the developed binders in the construction industry and drilling operations is found [14].

4. Summary
Technological processes for the production of grouting silicate binders based on mineral waste from the PBR were developed.

A binder made from a mixture of cement and PBR waste has a high sulfate resistance, especially hardening in hydrothermal conditions. In order to increase the quality and durability of binders made of these materials, it is recommended to seal the mixture with salt solutions and subsequent hydrothermal treatment. Products manufactured under these conditions on the basis of the studied binder have absolute resistance in an aggressive environment of sulfate mineralization. The proposed compositions and techniques for the preparation of grouting binders have high resistance in conditions of high temperatures, pressure and aggressive environment, simulating the working conditions when laying drilling wells.

5. References
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