Structure and properties of the cement stone modified by ultradispersed quartz waste

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Abstract. The paper scrutinizes the application of an ultradispersed filler from activated quartz waste as a modifier of cement stone and resulting physicomechanical characteristics of the latter. The deliverables justify the addition of the ultradispersed filler to cement stone in production of cement concrete. The physicomechanical characteristics of quartz-cement stone after dry and wet activation are given. Goal: the goal of the present work is to study the physicomechanical properties of the cement stone modified by ultradispersed quartz filler. Methodology: mechanical milling is used to get ultrafine particles. Research results: the research establishes that the effective ratio of ultradispersed activated quartz to cement is 30:70. The application of the ultrafine filler based on activated quartz waste allows increasing the density by 7%, strength by 35% and lowering the heat conductivity by 16%. Practical use of results: the work proposes a method for producing cement stone with augmented physicomechanical properties using quartz waste in the amount of 30% in total cement volume. Value: the work scientifically justifies the possibility to produce cement stone under hydraulic activation with denser structure with the major volumetric fraction of the filler represented by quartz waste particles with dimensions less than 20 μm.

1. Introduction
One of the most abundant minerals in the earth crust is quartz which is also a top-priority object of study by geologists for industrial application.
Unfortunately, the information on the world’s stock and production rates of quartz is not published, which is particularly connected with its strategic importance. It is believed that the quartz stock is fairly large. The main producers of natural quartz are known to be Brazil, Russian Federation and PRC.
There are 13 quartz fields in Russia with quite uneven distribution of the reserves along the state territory: 77.6% are in Ural Federal District, 16.5% in Siberian Federal District and 5.9% in Northwestern Federal District. Interestingly, a lot of fields are not accounted by the state register of mineral resources.
There is a plant producing ultrapure quartz concentrate—Polyarny kvarts, OJSC (Polar Quartz)—in Nyagan city of Khanty-Mansiysk Autonomous Okrug – Yugra. The project is of tremendous socio-economic value and develops two municipal formations of the Beryozovsky District: Ust-Puiva settlement (intermediate terminal with primary enrichment facility for quartz ore) and Nyagan city (plant for producing ultrapure quartz concentrate).
Quartz waste is a side product of quartz feedstock processing and amounts to 30% of total pure quartz concentrate production. One of the demanded solutions for utilization of a non-demanded product of the plant is production of high-strength small-grain concrete on the basis of ultradispersed quartz waste after production of ultrapure quartz concentrate.
2. Research methods
The work considers application of waste after ultrapure quartz concentrate production as an ultradispersed filler for production of nanostructured concrete with high physicomехanical properties. The physical model of nanostructured cement stone is given in Figure 1.

![Figure 1. Nanostructurization of cement stone: 1 - cement particles; 2 - ultradispersed quartz waste; 3-hydration products of clinker components.](image)

The main goal of the research was to investigate the effect of the filler based on ultradispersed quartz waste on the physicomехanical properties of cement stone.
To reach the goal, a structural scheme of the work was elaborated (Figure 2) which envisaged the investigation of secondary quartz waste application as an ultradispersed filler to produce concrete from a nanostructured cement gel. The gel was obtained using various ultradispersed quartz waste: 1) dust from on-site suction system (3–6 μm); 2) powder classification residue (6–7 μm); 3) grit magnetic separation waste (25–26 μm).

| Quartz waste | Primary | Secondary |
|--------------|---------|-----------|

| Application in construction (Industrial and road construction) | Activation type | |
|---------------------------------------------------------------|-----------------|--|
| 1 | 2 | 3 | No activation | Dry activation | Wet activation |

| Ratio of quartz waste mass to cement mass [%] |
|---------------------------------------------|
| 0:100 | 10:90 | 20:80 | 30:70 | 40:60 |

| Physicomechanical properties of cement stone (28-day cement stone: average density \( p_{av}, \text{g/cm}^3 \); heat conductivity \( \lambda_{av}, \text{W/(m·K)} \); compression strength \( R_{comp}, \text{MPa} \)) |
|----------------------------------------------------------------------------------------------------------------------------------|
| Figure 2. Structural scheme of investigation. |

The following materials were used in the study:
1. Binder (PTs-400-D20 cement).
2. Quartz waste after production of ultrapure quartz concentrate (Polyarny kvartz, OJSC). Secondary waste: Residues of grit magnetic separation, powder classification and dust collection (3–26 μm).

3. Tap water.

The specific surface and average size of the particles was determined by PSKh-12 device (Russia). The data is given in Table 1.

### Table 1. Physicomechanical properties of quartz waste.

| Property to be determined | Waste name | 1) Dust from on-site suction system | 2) Powder classification residue | 3) Grit magnetic separation residue |
|--------------------------|------------|------------------------------------|---------------------------------|-----------------------------------|
| Activation technology    | No activation | Dry | Wet | No activation | Dry | Wet | No activation | Dry | Wet |
| D (particle size) (μm)   | 3–6 | 2–4 | 1–3 | 7–11 | 4–7 | 3–5 | 25–29 | 17–20 | 13–15 |
| Ue (specific surface) (cm²/g) | 8017–4052 | 9547–5579 | 10860–8017 | 3249–1817 | 4815–3249 | 8115–4317 | 858–501 | 1951–1575 | 2360–2235 |
| ρ (bulk density) (g/cm³) | 1.59–1.78 | 1.68–1.86 | 2.08 | 1.55–1.69 | 1.75 | 2.07 | 1.73–1.83 | 1.55 | 1.87–1.99 |

The specimens were produced from cement slurry with normal viscosity and water consumption of 100 ml per 400 grams of cement. The strength of the quartz-cement stone was determined using nine specimens with dimensions of 2x2x2 cm for each composition, according to the structural investigation scheme. The parameters of the tests are presented in Table 2.

### Table 2. Physicomechanical properties of specimens

| Type of quartz waste (Secondary) | Activation technology | Physico-mechanical properties | Ratio of quartz waste mass to cement mass (%) |
|---------------------------------|-----------------------|-------------------------------|---------------------------------------------|
|                                 | Initial (no activation) |                               |                              | Absolute value | 10:90 | 20:80 | 30:70 | 40:60 |
|                                 | Dry activation         |                               |                              | Obtained results | Absolute value |
|                                 | 1) Dust from on-site suction system (Figure 4.4) | Density ρav (kg/m³) | 2397 | 2435 | 2451 | 2470 | 2491 |
|                                 | | Calculated porosity Pc (%) | 4.76 | 4.63 | 4.45 | 4.26 | 4.17 |
|                                 | | Heat conductivity coefficient λav (W/m K) | 0.406 | 0.396 | 0.388 | 0.381 | 0.377 |
|                                 | | Compression strength Rcomp (MPa) | 64.7 | 67.9 | 77.1 | 82.1 | 71.9 |
|                                 | Wet activation         | Density ρav (kg/m³) | 2401 | 2437 | 2455 | 2474 | 2495 |
|                                 | | Calculated porosity Pc (%) | 4.73 | 4.61 | 4.41 | 4.23 | 4.15 |
|                                 | | Heat conductivity coefficient λav (W/m K) | 0.405 | 0.395 | 0.386 | 0.379 | 0.376 |
|                                 | | Compression strength Rcomp (MPa) | 65.1 | 68.1 | 77.6 | 82.6 | 72.4 |

Continuation of Table 2:

| Physico-mechanical properties | Ratio of quartz waste mass to cement mass (%) |
|--------------------------------|---------------------------------------------|
| 10:90 | 20:80 | 30:70 | 40:60 |
| Absolute value | Obtained results | Absolute value |
| 100% | 102% | 103% | 104% |
| 97% | 96% | 94% | 93% |
| 101% | 102% | 104% |
| 97% | 93% | 89% | 88% |
| 100% | 105% | 112% | 111% |
| 102% | 105% | 105% |
| 98% | 95% | 94% | 93% |
| 100% | 105% | 105% | 105% |
| 97% | 93% | 89% | 88% |
| 100% | 105% | 105% | 105% |
| 102% | 105% | 105% | 105% |
| 97% | 93% | 89% | 88% |
| 100% | 105% | 105% | 105% |
| Type of quartz waste (Secondary) | Activation technology | 0: 100 Absolute value | 10:90 | 20:80 | 30:70 | 40:60 | Obtained results % of absolute value |
|---------------------------------|-----------------------|-----------------------|-------|-------|-------|-------|-----------------------------------|
| **Initial (no activation)**     |                       |                       |       |       |       |       |                                   |
|                                 | Density $\rho_{av}$ (kg/m$^3$) | 2387                  | 2426  | 2443  | 2461  | 2481  | 100%                              |
|                                 |                       | 100%                  | 101%  | 102%  | 103%  | 104%  |                                   |
|                                 | Calculated porosity $Pc$ (%) | 4.86                  | 4.71  | 4.55  | 4.35  | 4.26  |                                   |
|                                 |                       | 100%                  | 97%   | 94%   | 90%   | 88%   |                                   |
|                                 | Heat conductivity coefficient $\lambda_{av}$ (W/m K) | 0.404 | 0.394 | 0.386 | 0.379 | 0.375 |                                   |
|                                 |                       | 100%                  | 98%   | 96%   | 94%   | 93%   |                                   |
|                                 | Compression strength $R_{comp}$ (MPa) | 64.1 | 67.2  | 76.3  | 81.4  | 71.0  |                                   |
|                                 |                       | 100%                  | 105%  | 119%  | 127%  | 111%  |                                   |
| **Dry activation**              |                       |                       |       |       |       |       |                                   |
|                                 | Density $\rho_{av}$ (kg/m$^3$) | 2394                  | 2432  | 2447  | 2467  | 2488  |                                   |
|                                 |                       | 100%                  | 101%  | 102%  | 103%  | 104%  |                                   |
|                                 | Calculated porosity $Pc$ (%) | 4.80                  | 4.66  | 4.50  | 4.31  | 4.21  |                                   |
|                                 |                       | 100%                  | 97%   | 94%   | 90%   | 88%   |                                   |
|                                 | Heat conductivity coefficient $\lambda_{av}$ (W/m K) | 0.402 | 0.392 | 0.383 | 0.376 | 0.373 |                                   |
|                                 |                       | 100%                  | 98%   | 95%   | 94%   | 93%   |                                   |
|                                 | Compression strength $R_{comp}$ (MPa) | 64.7 | 67.9  | 77.1  | 82.1  | 71.9  |                                   |
|                                 |                       | 100%                  | 105%  | 119%  | 127%  | 111%  |                                   |
| **Wet activation**              |                       |                       |       |       |       |       |                                   |
|                                 | Density $\rho_{av}$ (kg/m$^3$) | 2421                  | 2494  | 2518  | 2566  | 2542  |                                   |
|                                 |                       | 100%                  | 103%  | 104%  | 106%  | 105%  |                                   |
|                                 | Calculated porosity $Pc$ (%) | 4.55                  | 4.28  | 4.05  | 3.96  | 3.91  |                                   |
|                                 |                       | 100%                  | 94%   | 89%   | 87%   | 86%   |                                   |
|                                 | Heat conductivity coefficient $\lambda_{av}$ (W/m K) | 0.379 | 0.345 | 0.330 | 0.322 | 0.318 |                                   |
|                                 |                       | 100%                  | 91%   | 87%   | 85%   | 84%   |                                   |
|                                 | Compression strength $R_{comp}$ (MPa) | 81.3 | 88.6  | 98.4  | 109.7 | 97.6  |                                   |
|                                 |                       | 100%                  | 109%  | 121%  | 135%  | 120%  |                                   |
| **Initial (no activation)**     |                       |                       |       |       |       |       |                                   |
|                                 | Density $\rho_{av}$ (kg/m$^3$) | 2378                  | 2417  | 2433  | 2451  | 2473  |                                   |
|                                 |                       | 100%                  | 102%  | 102%  | 103%  | 104%  |                                   |
|                                 | Calculated porosity $Pc$ (%) | 4.91                  | 4.75  | 4.59  | 4.41  | 4.3   |                                   |
|                                 |                       | 100%                  | 97%   | 93%   | 90%   | 88%   |                                   |
|                                 | Heat conductivity coefficient $\lambda_{av}$ (W/m K) | 0.401 | 0.391 | 0.383 | 0.374 | 0.370 |                                   |
|                                 |                       | 100%                  | 98%   | 96%   | 93%   | 92%   |                                   |
|                                 | Compression strength $R_{comp}$ (MPa) | 57.4 | 63.1  | 71.1  | 75.3  | 66.0  |                                   |
|                                 |                       | 100%                  | 110%  | 124%  | 131%  | 115%  |                                   |
| **Dry activation**              |                       |                       |       |       |       |       |                                   |
|                                 | Density $\rho_{av}$ (kg/m$^3$) | 2385                  | 2423  | 2439  | 2459  | 2478  |                                   |
|                                 |                       | 100%                  | 102%  | 102%  | 103%  | 104%  |                                   |
|                                 | Calculated porosity $Pc$ (%) | 4.85                  | 4.7   | 4.55  | 4.37  | 4.25  |                                   |
|                                 |                       | 100%                  | 97%   | 94%   | 90%   | 88%   |                                   |
|                                 | Heat conductivity coefficient $\lambda_{av}$ (W/m K) | 0.399 | 0.389 | 0.382 | 0.371 | 0.369 |                                   |
|                                 |                       | 100%                  | 97%   | 96%   | 93%   | 92%   |                                   |
|                                 | Compression strength $R_{comp}$ (MPa) | 57.9 | 63.6  | 71.6  | 75.9  | 66.4  |                                   |
|                                 |                       | 100%                  | 110%  | 124%  | 131%  | 115%  |                                   |
| **Wet activation**              |                       |                       |       |       |       |       |                                   |
|                                 | Density $\rho_{av}$ (kg/m$^3$) | 2433                  | 2482  | 2530  | 2555  | 2532  |                                   |
|                                 |                       | 100%                  | 102%  | 104%  | 105%  | 104%  |                                   |
|                                 | Calculated porosity $Pc$ (%) | 4.73                  | 4.45  | 4.21  | 4.12  | 4.07  |                                   |
|                                 |                       | 100%                  | 94%   | 89%   | 87%   | 86%   |                                   |
|                                 | Heat conductivity coefficient $\lambda_{av}$ (W/m K) | 0.375 | 0.341 | 0.326 | 0.319 | 0.315 |                                   |
|                                 |                       | 100%                  | 91%   | 87%   | 85%   | 84%   |                                   |
|                                 | Compression strength $R_{comp}$ (MPa) | 70.5 | 79.7  | 90.9  | 95.2  | 93.1  |                                   |
|                                 |                       | 100%                  | 113%  | 129%  | 135%  | 132%  |                                   |
The quartz waste was activated on a Viyuga-3 continuous rotary mill (Russia). The mill subjects the ultradispersed quartz materials to mechanical activation during dry milling, and to mechanical and hydrodynamic activation during wet milling (Figure 3).

### 3. Experimental

The specific surface of the filler is determined by the size, shape and roughness of its grains: the smaller they are, the larger the surface roughness and the specific surface of the filler grain are.

The weight distribution of secondary quartz waste particle size before and after activation was determined by a Microsizer 201 particle analyzer (Scientific Instruments, Russia). Below is the figure illustrating the weight distribution of particle size depending on the quartz waste type: Figure 4a depicts data for the dust from on-site suction system, Figure 4b, for the powder classification residue and Figure 4c, for the grit magnetic separation residue.

The structure of the specimens was studied by a REM 100U scanning electron microscope (Russia). The microphotographs (Figure 5) clearly depict needle-like crystals and their agglomerates that are typical for ettringite (calcium hydrosulfoaluminate). The prismatic crystals evidence the presence of alite, while rounded crystals indicate belite.

The images of the pore volume and pore walls clearly show the aggregates of well crystallized long-fiber hydroaluminate forming both at the interface of a pore and pore wall, and inside a pore. These crystallization contacts make up a rigid skeleton from fibrous (needle-like) crystals penetrating the porous volume of concrete, which improves its hardness and compression strength.

The analysis has detected calcium hydroxides crystallizing as elongated crystals and massifs (Figure 5c). Such massifs enhance heat conductivity.
The studies allow concluding that the component of the cement stone based on quartz waste finely milled down to 20 μm demonstrates its activity by building bridges binding it with the cement matrix and playing the role of discrete reinforcement. The presence of such needle-like build-ups may evidence increased strength of the material, because they play a reinforcing role in the concrete structure.

![Figure 5. Microstructure of cement stone using activated secondary waste of ultrapure quartz concentrate production a) grit magnetic separation residue; b) powder classification residue; c) dust from on-site suction system.](image)

The received results show that the higher the specific area of the micro-filler produced from the waste of ultrapure quartz concentrate production in Nyagan city is, the more actively it interacts with other hydration products via faster reaction forming finely dispersed hydrates.

4. Conclusion
The deliverables testify that the application of activated waste of ultrapure quartz concentrate production of the plant in Nyagan city allows saving up to 30% of cement.

The application of the ultradispersed filler based on activated quartz waste allows improving the physicomechanical properties of cement stone: increase the density by 7% and strength by 35%, decrease the heat conductivity coefficient by 16%.

Wet activation increases the strength of the specimens 1.5 times as compared to non-activated specimens. In contrast to dry milling, the strength of the specimens increased 1.3 times.

The study of the implementation of the activated quartz waste as an ultradispersed quartz-cement binder yielded the effective ratio of quartz to cement (30:70) applicable in both industrial and civil construction. Assumably, the industrial implementation of received results will attract considerable amount of investments in Khanty-Mansiysk Autonomous Okrug, which will positively affect economic and social situation in the region and solve local ecological problems.

This will reduce expenses for production of pure quartz and basic cost of quartz concentrate, improve the competitive ability of the products and reduce the environmental footprint of the plant, because the production waste requires disposal activities, expenses for packaging, temporary storage, transportation to disposal field, field maintenance and land remediation.

5. References
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