Influence of silica-containing materials surface properties on concrete structuring processes

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Abstract. The paper observes positive the influence of silica containing materials on cement systems. Practical and ecological parameters are shown. The data of a number and types of exchanges centers resulted from milling of industry-related materials are reported. Analysis of exchanges centers influence on cement hydration activity and "cement-mineral surface" contact zone interaction is provided. Theoretical justification of quartzitic sandstone and magnetic separation waste application as raw material for fillers is created. The influence of fillers surface on concrete structuring based on concrete plastic strength research is studied. It is determined that industry-related quartz-containing fillers application in amount 15 to 40% by weight of cement increases the plastic strength of cement paste and the speed of hydration processes. The period of structure formation of the cement stone is shortened, the intensity of hydrate accumulation processes increases. These data confirm the results of x-ray phase analysis of cement stone samples. A large amount of low and high basic capacity hydrosilicates is discovered during magnetic separation waste and quartzitic sandstone application. The use of the researched materials as fine fillers in cement concrete allows obtaining a composite with improved physico-mechanical characteristics and durability.

1. Introduction
Concrete is one of the most common building materials. This is due to the large number of concrete types and products that can be made from it. An important factor is the availability of the control mechanisms of the mixtures properties and the final product. The correct selection of components and the application of modifying additives allows one to obtain a material with specified characteristics that meets the requirements in various areas of construction.

2. Relevance of the issue
When choosing mineral raw materials for cement concrete, the main attention is paid to they granulometric composition, grain shape and surface morphology. These parameters are important in the selection of inert coarse aggregate. they main function is to create a solid framework in concrete for the perception of the load. However, fine aggregates and fillers have a much larger specific surface. This feature makes it possible to influence the structure formation processes in concrete at the macro and micro levels. [1,2]. If these materials have activity relative to cement, it is necessary to know the properties of they surface. Materials genesis and surface condition play significant role at cementitious material hydration process activation and concrete structuring [3].
for research in this area is the use of silica-containing fillers and mineral additives in the production of cement mortar and cement concrete [2,4-9].

It is known that the fillers have a positive effect on the physicomechanical properties of the creating cement stone: a tighter packing of binder particles, an increase in the number of contacts between the neoplasms, an acceleration of the initial stage of hardening of cement systems [4,10].

Research [11] observes that microfiller particles activate cement hydration processes. That is, they are crystallization centers for hydration products. At the same time, highly dispersed additives have a positive effect on the structure formation processes due to the high surface energy of their particles [5].

The use of raw materials with an active surface allows to intensify the processes in the contact area "cement- filler". Cement and aggregate Interface research is showed a more dense structure via the use of microsilica additives [4,8,12]. Improved adhesion at the interface affects the strength and durability of the composite [13,14]. At the same time, the adhesive properties of the cement with respect to the aggregates and fillers used must be taken into account.

Therefore, an important task is to find ways to increase the reactivity of the mineral materials surface used in cement concrete. This can be achieved by mechanical activation of the material during its grinding. [8, 15], due to the increase in the specific surface of the material and the number of active centers on it. Physical and chemical surface treatment is also widely used [7,16] as well as joint use of fillers with various surfactants [2,14,17].

Application of fine aggregates and mineral additives during concrete production has significant practical interest. Many studies have noted the possibility of replacing part of the cement with fine fillers without losing the strength of concrete or increasing it. [4,8,18]. The introduction of fillers in high-strength concrete becomes a necessity [5].

It should be mentioned that the use of fillers and mineral additives from technogenic raw materials partially helps to resolve the issue of recycling industrial waste, helps to improve the environmental situation. [1,2,6,14,17].

3. Aim
The aim of this work is to establish the influence of the silica-containing materials surface properties on the structure formation process of cement systems.

4. Materials and methods
Research objects are fine grained silica-contained mineral fillers, produced by milling of technogenic raw material, as quartzitic sandstone and magnetic separation waste. For comparison, milling quartz sand and sifting of granite from the Pavlovsky quarry were used.

The surface activity was estimated by the method of distribution of adsorption centers in the spectrophotometric version [19,20]. Structuring ability of fillers was determined by the method of conical plastometry. The phase composition of cement stone was investigated by infrared spectroscopic method.

5. Research results and discussion
One method of improving adhesion between cement and aggregate surface in concrete is to intensify the hydration processes of the cement in the contact zone. The active surface of the mineral components contributes to this effect. Studies indicate a significant difference in the surface activity of the studied materials. [21].

Table 1 presents data on the adsorption centers distribution of the research materials according to the total content of adsorption centers in a specific area of the pK, as well as their total number. From table 1 it can be seen that the greatest number of active centers is contained on the granite surface. In this case, the main contribution to make the Lewis base. It is known [22] that they are able to slow down the processes of cement hydration. On the surface of quartzitic sandstone and wet magnetic separation waste, the total number of active centers is less. However, about 50% of them are
Broensted acidic sites. The latter have a major impact on the cement materials hydration activity. A high content of Brønsted bases (34–38%), which increase the adhesion strength of cement stone with mineral materials, has been established [23]. Lewis acid sites on the surface of quartzitic sandstone and magnetic separation waste are 1.8-8.5 times more than on the surface of the other research materials. As can be seen from the above, the surface of quartzitic sandstone and wastes of wet magnetic separation of ferruginous quartzites should be the most active relative to cement.

Table 1. Adsorption site distribution on materials surface.

| Samples               | Adsorption site $10^3$, mg-eqv/m$^2$ at pHk | Lewis base | Broensted acidic sites | Broensted base | Lewis acidic | ∑ |
|-----------------------|---------------------------------------------|------------|------------------------|----------------|-------------|----|
| Quartzitic sandstone  | 1.88                                       | 24.62      | 18.21                  | 3.40           | 48.11       |    |
| Magnetic separation   | 5.52                                       | 22.30      | 15.78                  | 3.48           | 47.08       |    |
| waste                 | 27.40                                      | 21.10      | 11.34                  | 1.89           | 61.73       |    |
| Granite               | 7.39                                       | 9.00       | 8.70                   | 0.80           | 25.89       |    |
| Quartz sand           | 27.40                                      | 21.10      | 11.34                  | 1.89           | 61.73       |    |
| Granite               | 7.39                                       | 9.00       | 8.70                   | 0.80           | 25.89       |    |

The research results of the aggregates adhesion to cement stone, presented in [21], confirmed the assumptions made. Clear relationship between the number of aggregates surface acid centers, structure formation processes and adhesion in the contact zone is established. This is consistent with the results of N.N. Shanginoy [24]. Research shows that fillers with acidic centers (pKα from 0 to 7 and more than 12.8) sharply activate the hydration processes.

As can be seen from the above, fine aggregates and fillers from quartzitic sandstone and waste MMC provide the highest adhesion to the cement from the researching materials. They surface has maximum number of acidic active centers formed during genesis and technogenesis [25].

The influence of the technogenic raw materials fillers surface on the cement structure formation is determined. Research is based on the study of the plastic strength of the system "cement - filler". It is known, the mineral fillers application into cement systems intensifies the hydration processes of clinker minerals [4,5,26]. During portland cement hydration with present minerals of fillers, earlier periods of the formation of hydrate formations are observed. The intensity of hydrate accumulation processes increases.

Figure 1 shows the influence of researching mineral additives with a specific surface of 350 m$^2$/kg on the process of cement systems structure formation. Plastic strength was determined using a conical plastometer (the angle at the apex of the cones was 300) with a filler content of 15 and 40%.

![Figure 1](image-url)  

**Figure 1.** Plastic strength kinetics of cement paste with 15% (a) and 40% (b) filler: 1 – magnetic separation waste; 2 – quartzitic sandstone; 3 – quartz sand; 4 – granite; 5 – cement.
From the data presented, it is clear that the researching materials have a structuring effect. With the filler application at the system, cement paste plastic strength significantly increases. With increasing of the filler amount, structuring time is reduced and the rate of hydration processes increases. These results are consistent with the data [4]. Two characteristic areas on the kinetic curves can be distinguished. The first section is characterized by a slight increase in structural strength. It corresponds to the induction period of cement hydration. During this period, the mixture retains the properties of a structured liquid. In the second area, a sharp increase in structural strength is observed. This is due to the transition of the cement paste from the coagulation system to a rigid structure. For samples containing 15% filler, the first period is 170–200 minutes from the time of mixing with water. With an increase in the content of filler in the system to 40%, the onset of the second period occurs in 165–190 minutes. The growth of plastic strength in the second section is more intense. The curves show a pronounced inflection, which characterizes the transition from one section to another. That is, as a result of the manifestation of surface forces, the filler changes the mobility of the mixture and shortens the period of structure formation (cement setting time). The greatest structuring effect is observed when using magnetic separation waste and quartzitic sandstone. The presence of active adsorption centers significant number on their surface provides interaction with cement paste. The active influence of the quartzitic sandstone surface and magnetic separation waste on the structure formation processes and on the cement phase composition is confirmed by the X-ray phase analysis results (Figure 2). This statement is based on increase in intensity of the lines corresponding to the products of hydration: calcium hydrosilicates of low (2.30; 2.46; 3.36; 4.26 Å) and high (1.83 Å) basicity. At the same time, there is a decrease in the portlandite amount, which is the cause of concrete sulfate corrosion. (1,93; 2,63; 4,93Å).

![Figure 2. X-ray diffraction pattern of hardened cement paste at contact zone of concrete aggregate: 1 – magnetic separation waste; 2 – quartzitic sandstone; 3 – granite; 4 – quartz sand; 5 – cement without concrete aggregate.](image)

6. Conclusion
The obtained results show that the aggregates and fillers of silica-containing raw materials have an active influence on the structure formation processes in the contact zone and phase composition of the cement stone. The active structuring effect of the researching quartzitic fillers and magnetic separation waste was revealed. It consists in reducing formation period of the structure, increasing the
plastic strength and the rate of structure formation. It is established that the high activity of silica-containing materials is associated with the maximum number of acidic active adsorption centers on the surface. All this allows to draw conclusions about the feasibility of using these materials as fine additives in the production of cement concrete.

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