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# Properties and Structure of Functional Concrete Mixtures Modified with River Shell Powder

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**Abstract**

The recycling of the aquaculture waste into clam powder reduces solid emissions and natural resources, which is important for Portland cement production. This study determines the feasibility of using recycled river shell waste as a partial replacement for cement in concrete technology. The study used normative methods and optical microscopy; the properties of cement mixtures, such as normal consistency, setting time (ST), compressive and flexural strength, were studied. Research findings have shown that the inclusion of river shell powder (RSP) in cement mixtures can reduce water demand and a decrease in setting time with increasing RSP content. It was also found that the strength of the cement mixture can be maintained with an RSP content of up to 10%. The following properties of the concrete were determined: workability, compressive strength (CS), and water absorption. Using RSP as a partial replacement for cement has been proven to elevate the slump of the fresh concrete cone. CS is maintained at a level comparable to the control composition, with an RSP content of no more than 8%, and water-absorbing is reduced by 7.31%. This study created new compositions, and the links between the ingredients, properties, and structure of cement composites modified with river shell powder were investigated. Additionally, the properties of the structure-formation process of these modified composites were studied.

*Keywords:* Concrete Modifier; River Shells; Concrete Mixture; Cement Mixture; Compressive Strength; Flexural Strength.

## 1. Introduction

Currently, the global community is grappling with a range of environmental problems. One of the irrational practices involving natural resources is the inefficient utilization stemming from economic activities in diverse sectors [1-3]. Among the various economic activities, aquaculture stands out as a methodical cultivation of beneficial resources in the

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aquatic environment to serve crucial purposes for the population [4, 5]. This concept implies not only a careful attitude to the process of extraction and cultivation of special organisms, but also the correct disposal of accumulated waste due to the vital activity of such organisms or their extraction [6, 7]. Regarding aquaculture waste, the classification is very extensive and diverse. One of such wastes is river shells that accumulate near rivers [8, 9]. Aquaculture is the controlled cultivation of aquatic resources to benefit human needs. At the same time, several effective options are known in the scientific and practical literature, which involve the use of shells of various mollusks in waste-free technologies as a component of a beneficial effect aimed at other purposes [10, 11].

The manufacturing of construction materials is an important and sought-after approach for managing various forms of waste. Aquaculture waste is no exception. Previously, scientists around the world, including us, conducted research on the disposal of aquaculture waste in concrete, for example, river snails, mussels, scallops, and oysters. An illustration in El Mendili & Benzaama [12] demonstrates that incorporating up to 10% of powdered scallop shells in concrete does not impair the composite's characteristics while reducing environmental impact by up to 40%. In the study of Kim & Lee [13], the maximum amount of oyster shell waste powder that can replace cement in composites without compromising their properties is 25%. Similarly, in previous studies [14-16], adding finely ground powders from various shells instead of part of the binder component in optimal dosages enables the production of cement composites with improved physical properties without significant strength loss. Shellfish shell waste can also be used as large and small aggregates in cement concrete while maintaining their required properties [17–19].

However, the research on the combination of concrete at the fundamental level, as well as at the level of formation of concrete properties, has not been sufficiently studied [20, 21]. Of particular interest is the structure formation process of composites modified with powders of waste shells of various mollusks. This process is a complex, fundamental, and applied problem [22-24]. Finely ground river snail powder can be classified as carbonate additives, which in turn are mainly considered inert fillers [25, 26]. However, with increasing grinding fineness, a certain proportion of particles of this additive enter into a hydration reaction, thereby influencing the process of structure formation [27, 28]. New crystallization centers are formed in the form of calcium bicarbonates, calcium hydro-carbo-aluminates, and calcium-hydroxy-aluminates [29, 30]. The CSH (calcium hydrosilicate) phase silicates of Portland cement interact with carbonate additives, leading to their formation with the formation of $Ca(HCO_3)_2$, which decomposes into calcium bicarbonate and bicarbonate ions $CaHCO_{3+}$ and $HCO_{3-}$ [31, 32]. Accordingly, the structure and strength of cement composites modified with additives with a high content of calcium carbonate will largely depend on their particle size distribution and reactivity [33].

It should be noted that there were several studies that have comprehensively reviewed the use of seashells in concrete [34, 35]. In these studies, attention was paid to such characteristics of concrete as mechanical properties, durability, and microstructural characteristics [34, 36-38]. The thermal properties of such concrete have also been studied in separate works [39]. Shells are used in concrete as a replacement for part of the binder and aggregate [34, 37, 38, 40]. There are many studies describing the use of seashells, while river shells have been poorly studied. However, large amounts of aquaculture waste in the form of shells also accumulate in rivers, which is also a problem [17]. Their use in concrete will partially solve this problem. Thus, the study aims to close the gap in effective application of waste river shells in concrete.

Therefore, it is crucial to understand how modifying cement composites with river shell powder affects them. At the application level, it is important to understand the real relationship between the properties of cementitious composites, their manufacturability, and the ability to apply new knowledge as a useful engineering problem. It is important to note that there is a lack of research focused on studying the process of composites' structure formation when modified with shell powder.

In this study, for the first time, new compositions were created, and the links between the ingredients, properties, and structure of cement composites modified with river shell powder were investigated. Additionally, the properties of the structure formation process of these modified composites were studied. The purpose of this investigation is to examine the possibility of using recycled waste river shells as a replacement for part of the binder in the technology of cement composites, as well as the influence of this additive on the process and features of structure formation. The objectives of the work are:

- Studying the possibility of micro modification of cement mixtures and concretes with river shell powder, determining the effect of such micro modification on their properties;
- Comparison of the results obtained with results in similar industries, for example, by comparing the effectiveness of shell powder with other aquaculture waste.
- Finally, proposals for future scientific research and practical industry development, including production and aquaculture, are presented.

## 2. Materials and Methods

### 2.1. Materials

The selection of materials is crucial for research due to its complex fundamental and applied nature. It is vital to find out the essential nature of structure formation in concrete modified with finely ground river shell powder. In this regard, the choice of materials is determined by the choice of cement and mixer, that is, water, which will stabilize the controlled indicators at the same level. It is crucial to consider the approach taken when dealing with inert components. Using inert materials to study cement mixtures and concretes is justified as it ensures maximum neutrality and purity of the experiment's parameters [41, 42].

A standard set of raw materials was used to manufacture the samples. Portland cement CEM I 52.5N (PC) (CEMROS, Stary Oskol, Russia) was used as a binding component. Polyfractional sand (PS) (Eurostroykomplekt, Donetsk, Russia) was used to produce samples of cement mixtures. And quartz sand (QS) (Arkhipovsky quarry, Arkhipovskoye, Russia) and granite crushed stone (CrS) (Granit, Kamennogorskoye, Russia) were used as fine and coarse aggregates for concrete. The properties of the main components of the combination of concrete are presented in Table 1. For crushed stone particles and sand, the size distribution curves are displayed in Figure 1.

**Table 1. Properties of raw materials**

| Raw material | Indicator | Actual value |
|---|---|---|
| PC | Specific surface area ($m^2$/kg) | 346 |
| | Ability to pass through a screen No. 008 (%) for fineness | 99.1 |
| | Time settings (min)<br>- start<br>- end | <br>145<br>225 |
| | Compressive strength (MPa):<br>- 2 days<br>- 28 days | <br>23.5<br>56.4 |
| QS | Density of bulk (kg/$m^3$) | 1342 |
| | Apparent density (kg/$m^3$) | 2611 |
| | Quantity of dust and clay granules (%) | 0.06 |
| | Lump clay content (%) | 0.05 |
| | Contaminants and organics (%) | No |
| CrS | Bulk density (kg/$m^3$) | 1431 |
| | Apparent density (kg/$m^3$) | 2648 |
| | Limitation of fragmentation (wt %) | 11.2 |
| | Lamellar and acicular grain content (wt%) | 8.1 |
| PS | Silicon oxide content $SiO_2$ (%) | 98.7 |
| | Humidity (%) | 0.1 |

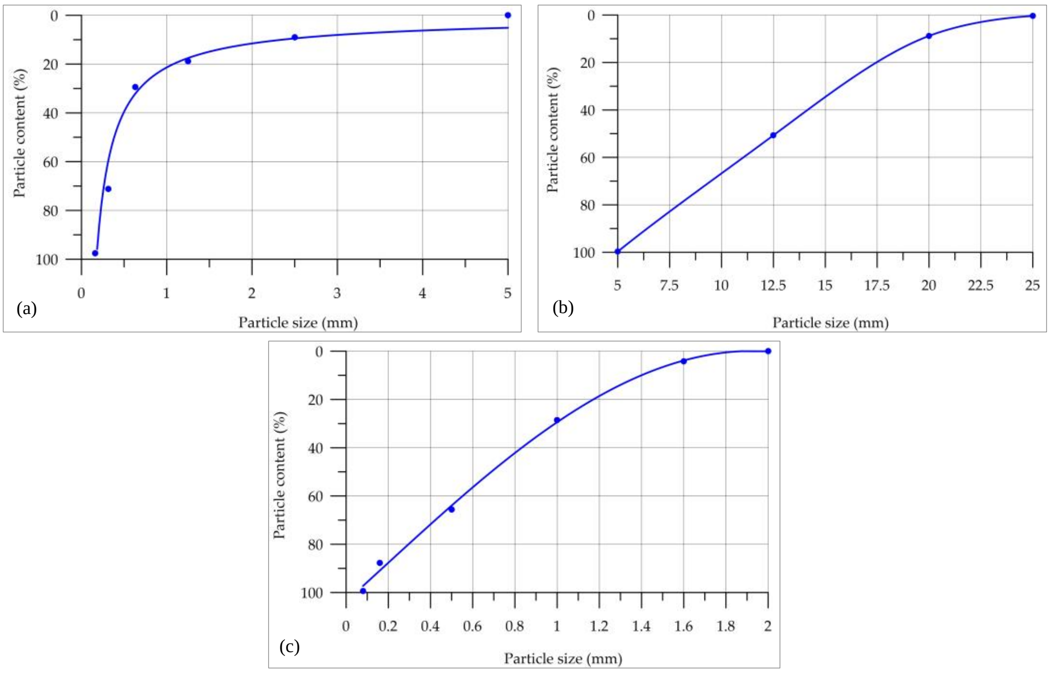



**Figure 1. Distribution curves of particle sizes (a) QS; (b) CrS; (c) PS**

River shell powder (RSP) collected on the banks of the Don River was used as a modifying additive, substituting part of the cement. The appearance of river shells and powder made from them is indicated in Figure 2.

(a) (b)

**Figure 2. Appearance of RSP: (a) after washing; (b) after grinding when added to combination of concrete**

With an Oxford Instruments X-Max 80 X-ray microanalyzer, the ZEISS CrossBeam 340 is a scanning electron/ion microscope. This instrument, manufactured by Carl Zeiss AG in Jena, Germany, allows for the chemical analysis of RSP. The chemical composition of RSP is provided in Table 2. RSP's bulk density is equal to 1309 kg/m$^3$.

**Table 2. Composition of RSP's chemicals**

| Element | Amount (%) |
|---|---|
| $SiO_2$ | 1.07 |
| $Al_2O_3$ | 0.15 |
| $Fe_2O_3$ | 0.06 |
| MgO | 0.04 |
| CaO | 61.11 |
| $SO_3$ | 0.14 |
| $SO_4$ | 0.06 |
| $Na_2O$ | 0.38 |
| $K_2O$ | 0.03 |
| CI | 0.01 |
| LOI | 36.95 |

Figure 3 illustrates the plot of the RSP particle size dispersion curve.

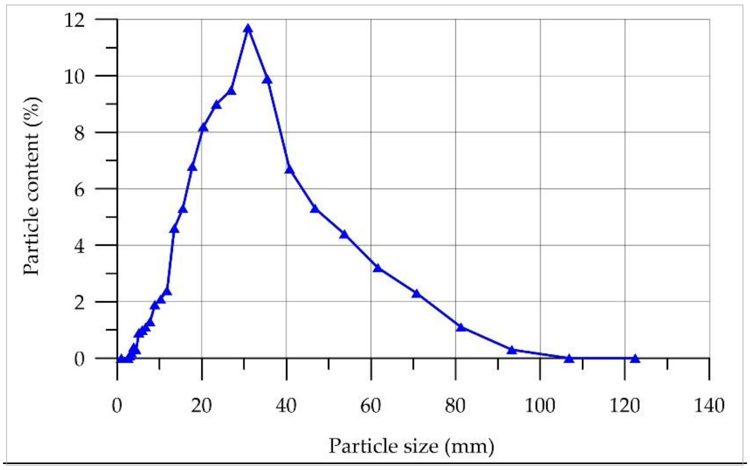



**Figure 3. RSP particle size distribution curve**

From Figure 3 the majority of RSP particles, namely 81.4%, are in the size range from 13.5 μm to 53.7 μm with a distribution peak of 11.7% at 31 μm.

Next, Figure 4 shows the RSP diffraction pattern. Using radiation from a copper anode, X-ray phase analysis was carried out using a DRON-7 diffractometer (NPP Burevestnik, St. Petersburg, Russia).

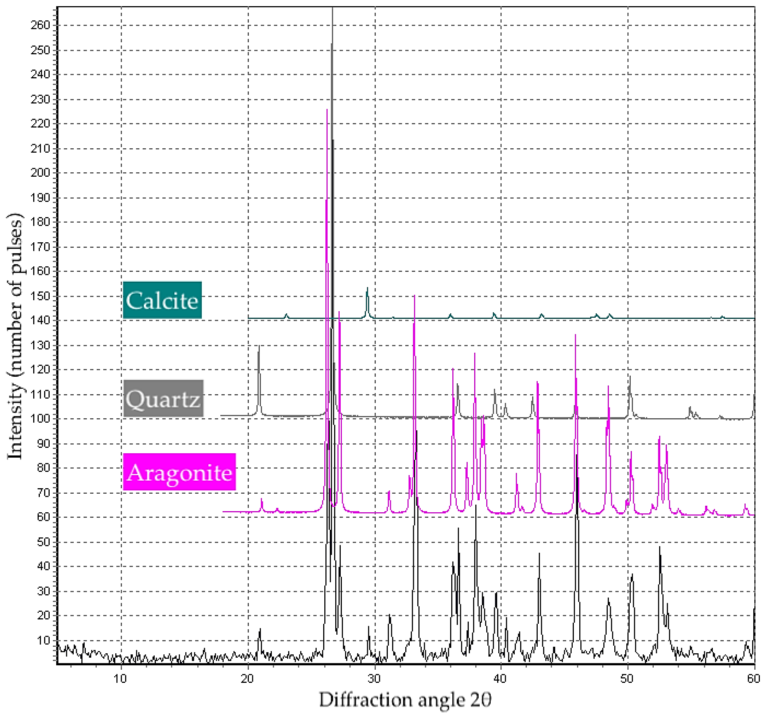



**Figure 4. RSP X-ray diffraction pattern**

Based on the results of X-ray phase analysis of RSP, phases such as calcite, quartz and aragonite were identified.

## 2.2. Methods

From the point of view of the techniques employed, it is important to match the principle of uniformity and repeatability in order to study the processes of structure formation, which can be classified as fundamental research, and then the processes of investigating the properties of cement mixtures. To proceed, we need to examine the feasibility of the combination of concrete, as it is the final product that determines the practicality of our research on modifying concrete with finely ground river shell powder. The last step is to examine the properties of the concrete that has been produced. That is, methodologically, the research can be presented in a step-by-step algorithm: "structure formation, cement mixture, combination of concrete, hardened concrete." At each research level, a unified methodological approach should be used to ensure repeatability and purity of the experiment. It is necessary to exclude the impact of the human factor and other uncontrolled parameters, and if it is impossible to exclude these factors, it is important to strive to minimize their influence in a negative way on the result of the experiment [43, 44]. In case of obtaining important new results, it is necessary to repeat this experiment at least three times in order to exclude accidental loss of results from the general series. Thus, in addition to laboratory experimental methods, it is also necessary to apply methods of mathematical statistics and mathematical processing of results. This approach to the methodology and to the phenomenological research model will allow us to determine fundamental and applied results within the framework of the assigned tasks [45, 46]. A workflow flow chart that briefly demonstrates the process of applying the research methodology is presented in Figure 5.

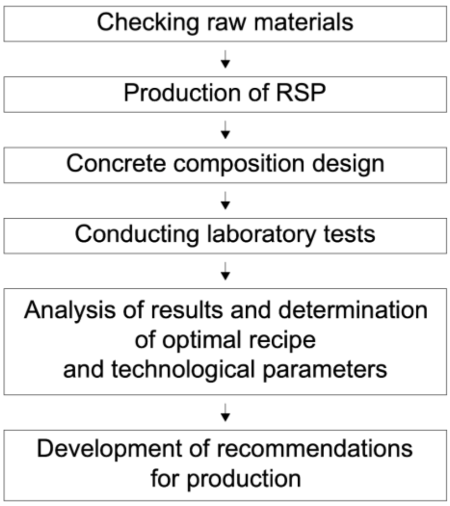



**Figure 5. Workflow Flowchart**

The RSP modifying additive was prepared as follows. The shells collected on the river bank were soaked for 24 hours, and then washed under running water and dried in a laboratory drying cabinet ShS-80-01 SPU (Smolensk SKTB SPU, Smolensk, Russia). To eliminate organic matter, washed and dried river shells were calcined in a SNOL 6.7/1300 muffle furnace (AB “UMEGA GROUP”, Utena, Lithuania) at 300 °C for 2.5 hours. The river shells were pulverized using a laboratory jaw crusher and subsequently refined into a fine powder using an Activator-4M planetary ball mill operating at a speed of 800 revolutions per minute for a duration of 20 hours.

Initially, the study focused on evaluating the potential of using a modifying additive from RSP in cement mixtures for concrete technology. The research focused on studying properties such as normal consistency, setting time, and compressive strength (CS) and bending strength of cement mixtures. The investigation of these cement mixture properties followed the guidelines of the methodology [47].

The Vika OGTS-1 gadget (RNPO RusPribor, St. Petersburg, Russia) was used to test the consistency of cement mixture with varying RSP contents. A sample of cement mixture was prepared using a laboratory mortar mixer Matest E093 (Matest, Treviolo (BG), Italy). Initially, an appropriate quantity of water was added to the mixer bowl to achieve a cement mixture with a standard consistency. Subsequently, cement and RSP were added according to the instructions provided in Table 3. All the ingredients were then mixed together for a duration of 90 seconds. The finished cement mixture was transferred to a ring mounted on a plate and filled completely, and the excess paste was cut off with a knife. Next, the ring with the plate was installed on the frame of the device and the rod was lowered, allowing the pestle to freely sink into the cement mixture. When the pestle did not touch the bottom of the plate by 6 ± 1 mm, the consistency of the cement mixture was deemed normal.

**Table 3. Mixture recipes for determining the normal consistency of cement mixtures**

| Mixture type | PC (g) | PS (g) |
|---|---|---|
| NC0 | 500 | 0 |
| NC5 | 475 | 25 |
| NC10 | 450 | 50 |
| NC15 | 425 | 75 |
| NC20 | 400 | 100 |

Vika OGTS-1 device (RNPO RusPribor, St. Petersburg, Russia) was chosen to determine the setting time (ST) of the cement mixture. Initially, a cement mixture of regular thickness was made and used to fill the ring. After the ring with the plate was installed, the rod was released, allowing the needle to freely plunge into the cement mixture. After immersion, the needle was raised and wiped with a damp cloth. This operation was repeated every 10 minutes until the needle, when penetrating the cement mixture, did not reach the plate by 4 ± 1 mm. The time from the beginning of setting until the moment when the needle did not reach the plate by 4 ± 1 mm was regarded as the commencement of establishment. The end of setting was the time from the beginning of cement mixing to the moment when the needle penetrated into the cement mixture no more than 0.5 mm. Testing of cement mixture samples is offered in Figure 6.


(a) (b)

**Figure 6. Testing of cement mixture samples with RSP: (a) normal consistency; (b) setting time**

To determine the CS and bending strength of the cement mixture, prism samples with dimensions of 40 × 40 × 160 mm were made according to the recipe presented in Table 4.

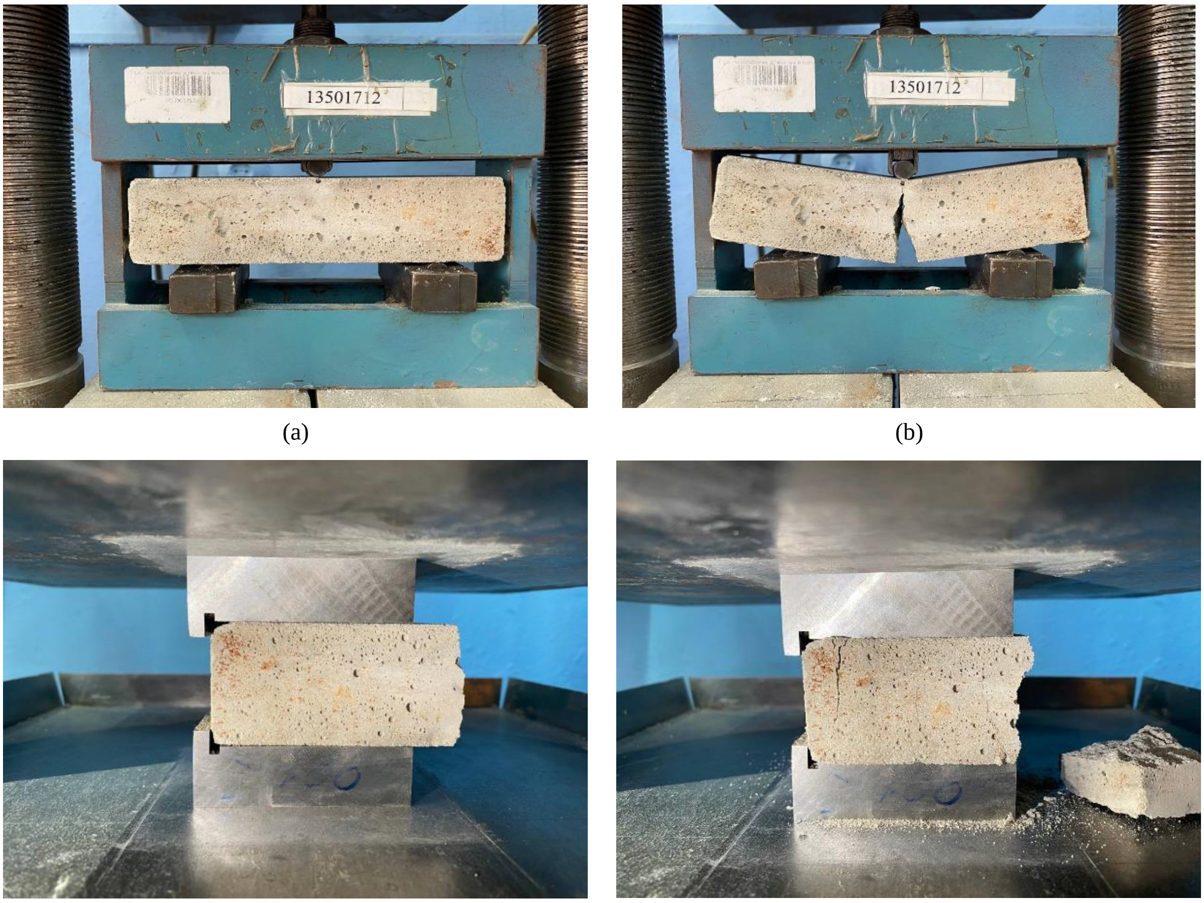
**Table 4. Formulation of cement mixtures**

| Mixture type | PC (g) | PS (g) | Water (ml) | RSP (g) |
|---|---|---|---|---|
| CP0 | 450 | 1350 | 225 | 0 |
| CP5 | 427.5 | 1350 | 225 | 22.5 |
| CP10 | 405 | 1350 | 225 | 45 |
| CP15 | 382.5 | 1350 | 225 | 67.5 |
| CP20 | 360 | 1350 | 225 | 90 |

The following technological operations were involved in producing the samples. Initially, the ingredients were measured as per the recipe. Then the solution was prepared by mixing all components in a laboratory mortar mixer Matest E093. From the prepared cement mortar, three portions of cement mixture, each weighing 300 g, were taken in turn with a spatula and filled with the first layer of the mold. After that, the cement mixture in the mold was leveled with a spatula and compacted on a shaking table with 60 blows. The second and third layers were compacted in a similar way, and excess cement mixture was removed with a ruler. The next step involved storing the prism samples in a standard hardening chamber for 24 hours before removing them from the molds. Once taken out of the molds, the samples were immersed in a water bath for 27 days. The matured samples of cement mixture were removed from the water, wiped with a damp cloth and tested. Determination of the bending strength of cement mixture samples was carried out as follows. First, the samples were mounted on the supports of the bending tester so that its forming faces were in a vertical position (Figures 7-a and 7-b). The distance among the supports is 100 ± 0.2 mm, and the rate of load increase is 50 ± 10 N/s. Flexural strength of cement paste ($R_{tb}$) was determined by the formula:

$$R_{tb} = \frac{1.5Fl}{b^3} \tag{1}$$

here $F$ is the breaking load (N); $b$ is length (mm) of the prism sample's side square section; $l$ is axial separation among the supports (mm).




(a) (b) (c) (d)

**Figure 7. Testing of cement mixture samples with RSP: (a), (b) $R_{tb}$ (c), (d) $R_{cp}$**

CS was determined by testing six halves of prism samples obtained during a bending strength test. To allow for the side faces of the prism sample, which were vertical when the samples were manufactured, to fit firmly against the plate stops, half of the sample was sandwiched between two plates to transfer the load to the sample (Figures 7-a and 7-d). A load increase of 0.6 ± 0.4 MPa/s observed throughout measurement. The cement paste's CS ($R_{cp}$) was determined by the formula:

$$R_{cp} = \frac{F}{S} \tag{2}$$

where $F$ is the breaking load (N); $S$ is the portion of the plate that is used for working ($mm^2$).

Six compositions were created to examine how RSP affects concrete properties. The compositions of combination of concrete with different RSP contents are presented in Table 5.

**Table 5. Recipe for combination of concrete**

| Mixture type | PC ($kg/m^3$) | QS ($kg/m^3$) | CrS ($kg/m^3$) | Water ($L/m^3$) | RSP ($kg/m^3$) |
|---|---|---|---|---|---|
| 0 | 360 | 711 | 1051 | 200 | 0 |
| C4 | 345.6 | 711 | 1051 | 200 | 14.4 |
| C8 | 331.2 | 711 | 1051 | 200 | 28.8 |
| C12 | 316.8 | 711 | 1051 | 200 | 43.2 |
| C16 | 302.4 | 711 | 1051 | 200 | 57.6 |
| C20 | 288 | 711 | 1051 | 200 | 72 |

The production of concrete samples with different RSP contents included the following technological operations. First, PC, QS, CrS, water and RSP were dosed according to the formulation. Next, PC, QS and RSP were loaded in dry form into a BL-10 concrete mixer (ZZBO, Zlatoust, Russia) and mixed for 60 seconds. Next, mixing water was added and the cement-sand mixture was mixed for 60 seconds. Subsequently, crushed stone was added to the mixture and thoroughly blended until it achieved a state of homogeneity. The finished combination of concrete was loaded into molds, which were compacted on a vibrating platform. Following a 24-hour period, the samples were extracted from the molds and placed in a standard hardening chamber until they reached maturity of 28 days.

Cone settling was used to assess the mixes' workability in compliance with the method's specifications [48]. A truncated cone-shaped compact was created using the provided a combination of concrete. The combination of concrete's workability was determined by the measured distance it settled when the cone was removed. To manufacture the sample under study, a metal cone with a smooth inner surface and the following internal dimensions was used: base diameter - 200 mm, top diameter - 100 mm, height - 300 mm. Before testing, the cone was wetted and placed on a flat, stable horizontal surface. The filling of the cone occurred in three separate steps. Each layer experienced equal distribution of impacts throughout its cross section. Throughout its entire thickness, the bottom layer was compacted, and there was no contact with the base by the bayonet. By compacting the middle-and upper layers completely, the impacts were able to penetrate into the underlying layer. The top layer was poured and compacted after the combination of concrete was put above the top edge of the cone. If the concrete settled below the cone's top edge during compaction, an additional mixture was included to sustain the level. Removing the excess from the surface of the combination of concrete followed the compaction of the top layer. The supporting surface was cleared of the spilled combination of concrete, and the cone was lifted carefully in a vertical manner to remove it. The time it took to raise the cone varied from 2 to 5 seconds. From start to cone removal, the entire process lasted 150 seconds with no interruptions. Following the cone's removal, the sediment was measured using the difference in height among the mold and the peak of the produced specimen.

The consistency of freshly mixed concrete changes over time due to cement hydration and/or possible loss of moisture, so to obtain exactly comparable results, tests were carried out on different samples at equal intervals after mixing.

Test results were considered positive only if a uniform slump was obtained, that is, a slump in which the combination of concrete was substantially undisturbed and symmetrical. If the test sample was displaced, the tests were repeated on another sample. Uniform settlement was recorded with an accuracy of 10 mm [48].

According to the guidelines of the procedures, the CS of samples of concrete was assessed [49-52]. All samples were tested on a Press P-50 installation (PKC ZIM, Armavir, Russia) at a constant load rate of 0.6 ± 0.2 MPa/s. The concrete's CS ($R_c$) was obtained using the formula below:

$$R_c = \alpha \frac{F}{A} \tag{3}$$

where $F$ is the breaking load (N); $A$ is sample working section area ($mm^2$); α is a coefficient taking into account the dimensions of the samples (for samples with a side of 100 mm $\alpha = 0.95$).

Specimens of concrete with RSP before and after failure are presented in Figure 8.

(a) (b)

**Figure 8. Determination of the $R_c$ of samples with RSP: (a) before failure; (b) after destruction**

he Water-absorbing of concrete samples was determined following the guidelines of regulatory documents [53, 54]. The samples were placed in a container filled with water so that the water level in the container was approximately 50 mm higher than the top level of the stacked samples. The samples were placed on spacers in such a way that the height of the sample was minimal. The water temperature in the container was maintained at (20 ± 2) °C. The samples were weighed every 24 hours of water absorption on a balance with an error of no more than 0.1%. Samples removed from water were first wiped with a wrung out damp cloth. The mass of water flowing out of the pores of the sample onto the scale was included in the mass of the saturated sample. The test was carried out until the results of two consecutive weighing differed by no more than 0.1%. The samples were tested in a state of natural moisture or in a dry state. The formula was used to determine the Water-absorbing ($W$) value:

$$W = \frac{m_W - m_d}{m_d} \times 100 \tag{4}$$

here $m_W$ is the mass of the sample saturated with water (g); $m_d$ represents is the mass of the dry sample (g).

The water absorption of concrete in a series of samples was determined as the arithmetic mean value of the test results of individual samples in the series.

Figure 9 illustrates the overall framework of the experimental study program.

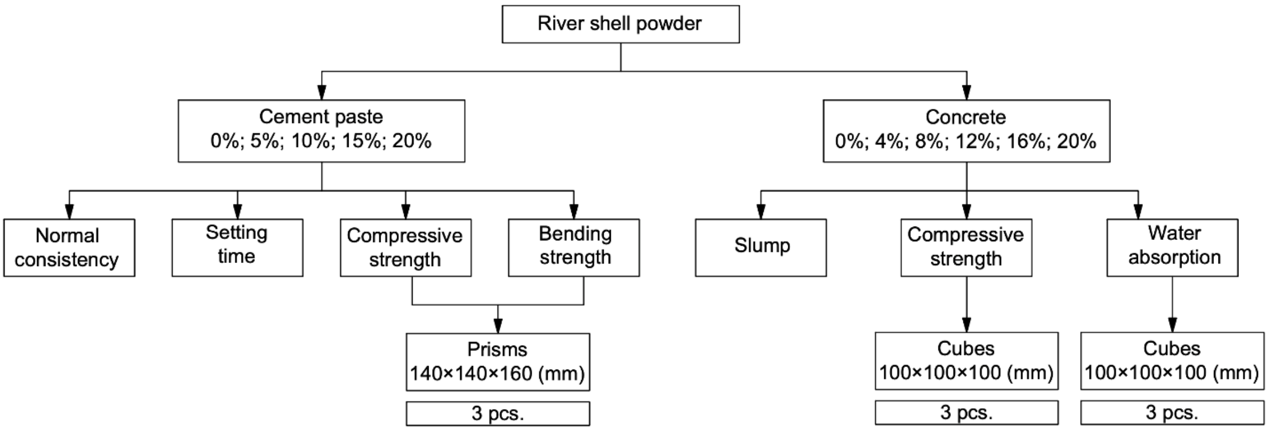



**Figure 9. Investigative research**

Thus, 15 prism samples of cement mixture and 36 concrete cube samples were made (18 to determine the CS and 18 to determine the Water-absorbing of concrete).

## 3. Results and Discussion

Figures 10 and 11 depict how variations in RSP content impact the normal consistency and ST of cement mixture.

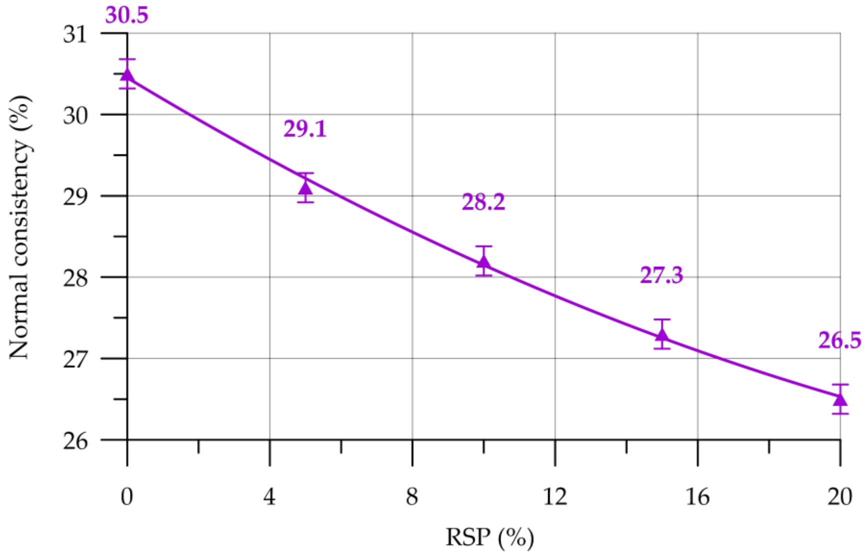



**Figure 10. Modification in the typical consistency of cement mixture with varying proportions of RSP**

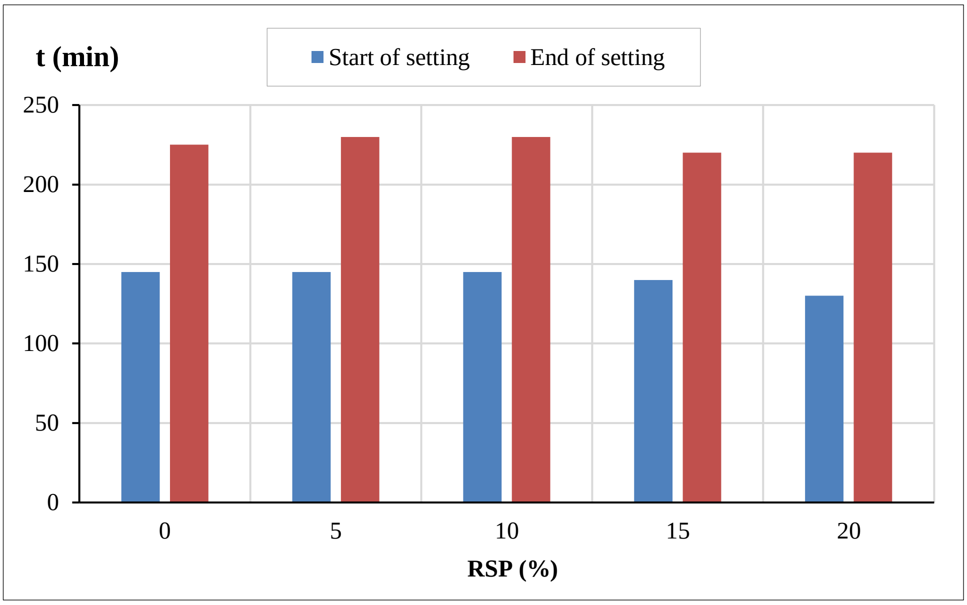



**Figure 11. Change in ST (t) of cement mixture at different RSP contents**

The standard deviation of normal consistency was up to 2%.

The dependence of the change in normal consistency (NC) on the amount of RSP, presented in Figure 10, is well approximated by Equation 5, where $x$ is the content of RSP in the mixture and $R^2$ is coefficient of determination

$$NC = 30.45 - 0.264x + 0.00343\,x^2, \qquad R^2 = 0.997 \tag{5}$$

It may be observed from Figure 10 that the water requirement of the binder reductions as the RSP content rises. At 5%, 10%, 15% and 20% RSP, Comparing the normal consistency values of the cement mixture to those of the control composition (without RSP), the cement mixture's normal consistency values dropped by 4.59%, 7.54%, 10.49%, and 13.11%. The reduction in water demand of cement mixture with the introduction of RSP is due to the fact that RSP particles have a dense, non-porous structure compared to cement particles. In addition, they exhibit less reactivity; therefore, less water is required for their wetting [35, 55]. The tendency to reduce the water demand of cement composites when substituting part of the binder with an additive in the form of river shell powder is also established by a number of other investigations [56, 57]. For example, in Wang and Liu [56], substituting part of the binder in cement mixtures with finely ground sea shell powder up to 40% helps increase the rheological features of cement mixtures by increasing the effective water-cement ratio, which can be significantly reduced when substituting a part of the cement with sea shell powder. shells, which indicates the lower water requirement of these mixtures. Similarly, in the study of Wang et al. [57], the introduction of sea shell powder up to 40% into the composition of the cement mixture allows to reduce their water demand.

Figure 11 shows that the addition of 5% and 10% RSP does not have a significant impact on the ST of cement mixtures. However, with a further increase in the RSP content, their decrease is observed. The decrease in ST with RSP contents of 15% and 20% in the cement mixture can be explained as follows. During the hydration of tricalcium aluminate ($C_3A$), the products of its hydrolysis bind the released $Ca(OH)_2$ and part of the calcium hydroxide ($Ca(OH)_2$) released during the hydrolysis of silicate minerals [30, 49, 51]. The hydration products of each $C_3A$ molecule bind an additional $Ca(OH)_2$ molecule from the liquid phase. Thus, the process of $C_3A$ hydrolysis can significantly accelerate the hydrolysis of tricalcium silicate ($C_3S$) and dicalcium silicate ($C_2S$) due to the binding of one of the reaction products $Ca(OH)_2$. The high speed of these reactions leads to a rapid setting of the cement mixture. The introduction of RSP actually leads to an acceleration of $C_3S$ hydration, especially in the early stages of hardening, which is explained by the formation of crystallization centers in the form of calcium bicarbonate, as well as the modified surface of tricalcium silicate [26, 31, 58, 59].

Next, Figures 12 and 13 present the results of determining CS and bending strength of cement mixture specimens with different RSP contents, respectively.

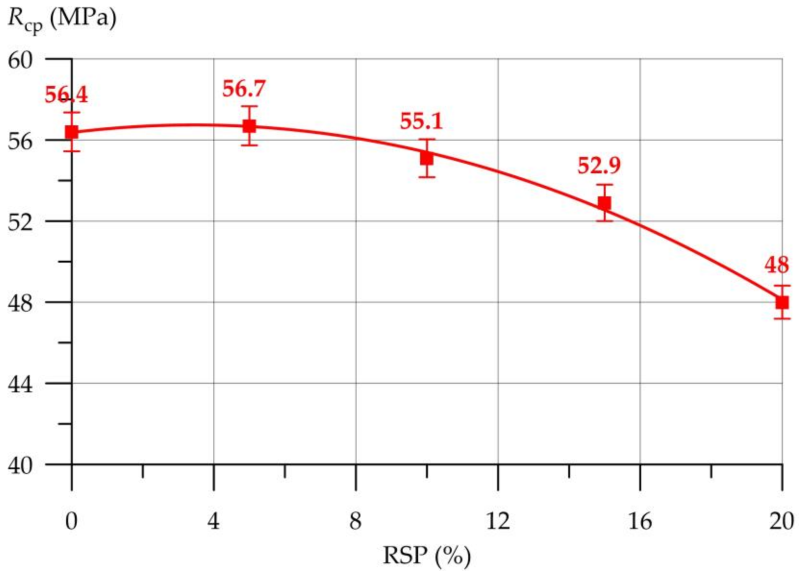



**Figure 12. Variation of cement paste CS ($R_{cp}$) with different RSP contents**

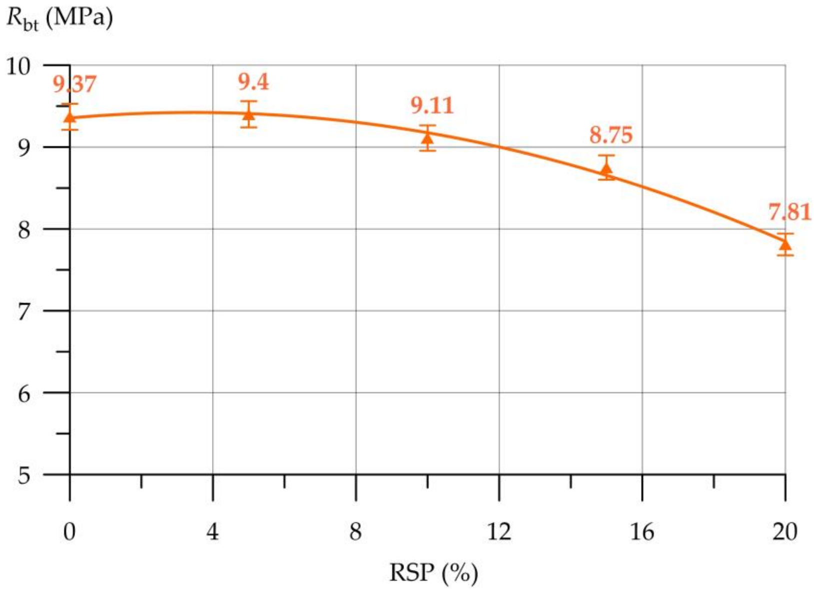



**Figure 13. Variation of flexural strength of cement paste ($R_{bt}$) with different RSP contents**

The standard deviation of $R_{cp}$ was up to 5%.

The standard deviation of $R_{bt}$ was up to 3%.

The changing strength characteristics' dependency $R_{cp}$ and $R_{bt}$ on the amount of RSP, presented in Figures 12 and 13, is well approximated by Equations 6 and 7, where $x$ is also the content of RSP in the mixture:

$$R_{cp}=56.36+0.2165x-0.03143\,x^2, R^2=0.995 \tag{6}$$

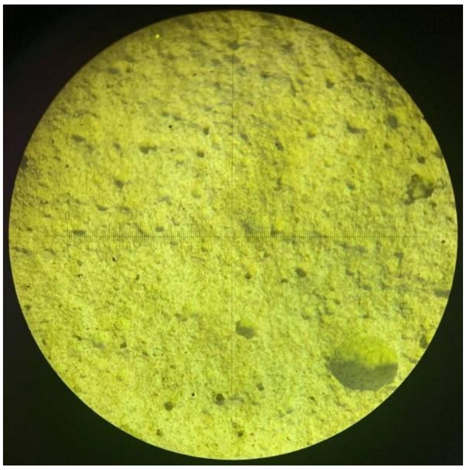
$$R_{bt}=9.354+0.0394x-0.00574\,x^2, R^2=0.991 \tag{7}$$

As can be seen from the results of assessing the CS of cement mixtures represented in Figure 12, an introduction of 5% and 10% RSP instead of part of the cement allows maintaining the CS at a level comparable to the control composition of the cement mixture. At a dosage of 5%, the CS of the samples is higher by 0.53%, and at 10% RSP, the CS is lower by 2.30% according to the composition of the control. Conversely, at a content of 15% and 20% RSP, a more significant decrease in CS is observed by 6.21% and 14.89%, accordingly, as compared to the composition under control.

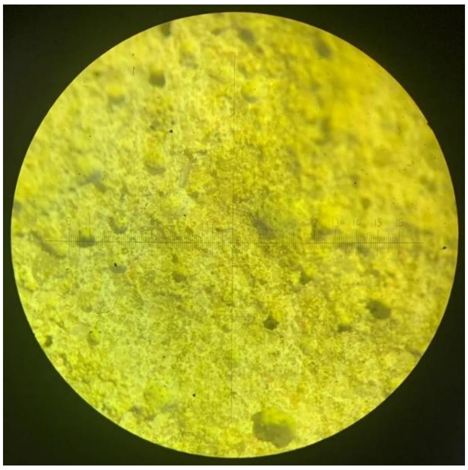
The flexural strength curve presented in Figure 13 is similar in nature to the CS curve presented in Figure 12. Substituting part of the cement with 5% and 10% RSP allows maintaining the flexural strength at the level of the control composition. At a content of 5% RSP, the increase in flexural strength was 0.32%, and at 10%, the flexural strength decreased by 2.77%. At 15% and 20% RSP, more significant reductions in flexural strength were observed, which were 6.62% and 16.65%, respectively. The preservation of the strength properties of cement mixtures with optimal dosages of additives from finely ground powders of various types of mollusks was also confirmed by many other studies [57, 59, 60]. To illustrate, in study [26], the substitution of up to 8% of the cement with oyster shell waste powder allowed for the preservation of the composite's properties at the desired level. At Han et al. [60], 5% was found to be the ideal replacement level of cement with oyster shell powder. Moreover, in this study, the optimal amount of RSP in the cement paste was found to be 5%, which is in good agreement with most of the studies studied. In addition, the improvement in the strength characteristics of pastes with the optimal amount of RSP is not inferior to the results of other studies and is within 10%. The explanation for the maintenance of strength properties in cement mixtures, even with the replacement of 5% and 10% of the cement with RSP, is as follows. Firstly, the RSP additive acts as a mineral filler, making the structure of the hardened cement mixture more uniform and denser. Also, this additive by its nature is carbonate-containing and affects the process of structure formation [57]. The chemical aspects of the formation of the strength of cement mixtures with RSP are explained by the formation of the following compounds:

- Calcium hydrocarboaluminates $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ and $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 30–32H_2O$ due to the interaction of calcite with tricalcium aluminate;
- Basic calcium carbonates $CaCO_3 \cdot Ca(OH)_2 \cdot mH_2O$;
- Tomasite $\{Ca_3[Si \cdot (OH)_6] \cdot 12H_2O\} \cdot (SO_4) \cdot (CO_3)$ [28].

Accordingly, the structure of cement mixtures with RSP in rational dosages has more densely packed aggregates of new formations and a smaller number of pores (Figures 14-a and 14-b). Photographs were taken using an MBS-10 optical microscope (Measuring equipment, Moscow, Russia) with 6x magnification



(a)



(b)

**Figure 14. Structure of cement mixtures: (a) control composition; (b) content 5% RSP**

The microscope images shown in Figure 14 should be discussed in terms of defects and potential cracks and failures. As can be seen when comparing the microstructures of standard and modified concrete, there are differences, expressed in a decrease in the number of defective areas in the structure of concrete at the microlevel in modified concrete. A decrease in the number of structural defects, namely a decrease in macro- and micro-porosity, voids, and structure breaks, indicates the positive effect of the modifier - RSP. RSP plays a role aimed at creating and strengthening additional crystallization centers, which helps improve the quality of the structure and reduce the risk of micro- and macro-cracks leading to concrete failure. As is known, cracks occur in places where internal stresses are concentrated, and this directly depends on existing structural defects. Based on the analysis, modified concrete with RSP will have greater resistance to cracking and premature failure than concrete of the control composition. Moreover, this assumption is valid both for short-term loads and for a long time.

Thus, based on the results of assessing the influence of RSP on the properties of cement mixtures, the following conclusions can be drawn:

- The use of RSP up to 20% instead of part of the cement helps reduce the water demand of cement mixtures;
- The use of RSP in a dosage of more than 15% reduces the ST of cement mixtures;
- The introduction of RSP in an amount of 5-10% does not have a significant effect on the strength properties of cement mixtures. The findings are very consistent with [58].

The findings of analyzing the characteristics of concrete produced using RSP are shown in Figures 15 to 17. The relationship between the slump of the combination of the concrete cone and the amount of RSP additive is depicted in Figure 15.

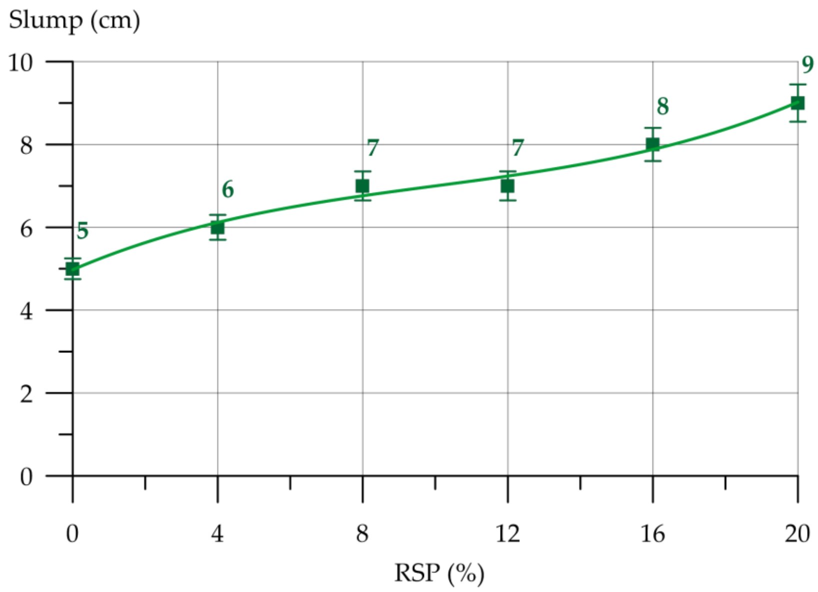



**Figure 15. Dependence of fresh concrete cone slump on the amount of RSP**

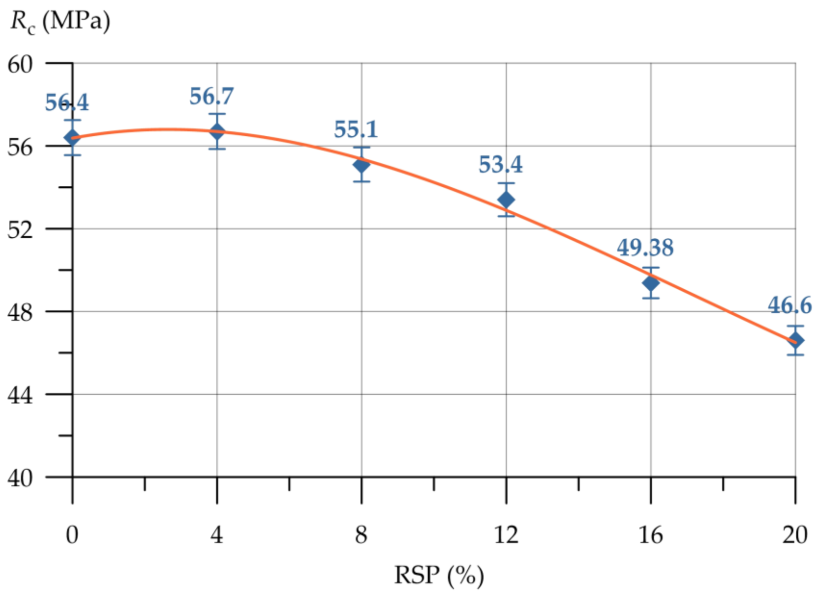



**Figure 16. Variation of concrete CS ($R_c$) depending on the amount of RSP**

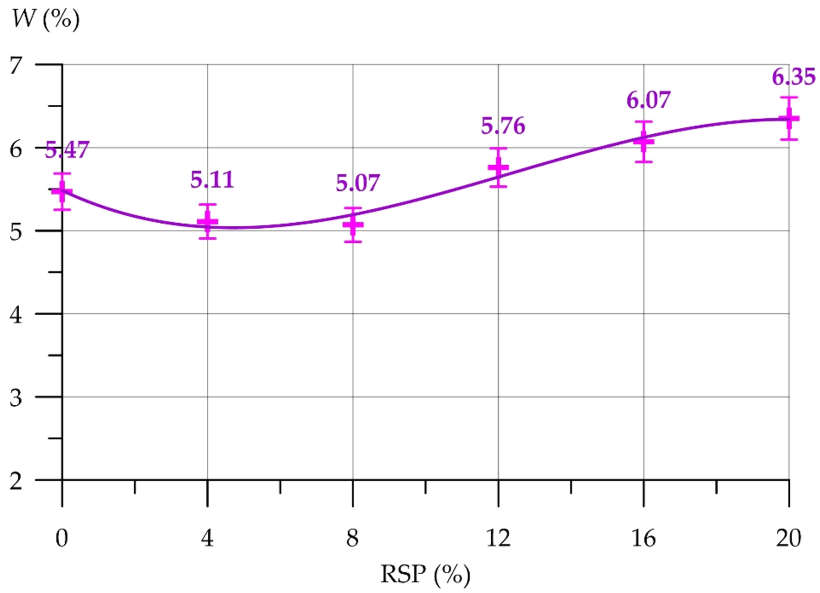



**Figure 17. Variation in Water-absorbing of concrete (W) based on the content of RSP**

The standard deviation of slump was up to 5%.

The dependence of the change in fresh concrete cone slump (*Sl*) on the amount of RSP, presented in Figure 15, is well approximated by Equation 8, where x is also the RSP content in the mixture

$$Sl = 4.976 + 0.376x - 0.0260\,x^2 + 0.000868x^3, R^2 = 0.985 \tag{8}$$

As can be seen from Figure 15, substituting part of the cement in combination of concrete with RSP from 4% to 20% promotes an increase in cone settlement as the percentage of replacement increases. The substitution of 4% caused a 1 cm rise in slump for the concrete mixture cone in comparison to the control composition. At 8% and 12% RSP, the cone settlement values are approximately equal, and their increases compared to the control composition are 2 cm. With the addition of 16% and 20% RSP, an increase in cone settlement by 3 cm and 4 cm, respectively, is also observed. The increase in slump of combination of concrete when substituting part of the cement with RSP is explained by the fact that RSP particles have a lower water requirement compared to cement particles. Also, RSP particles are largely inert, that is, most of them do not enter into a hydration reaction and act as a mineral filler [50]. At the initial stage of hydration, the cement gel has a weakly crystallized structure in the form of a flocculent mass of particles of various shapes. Adding RSP lowers the cement particle content, which dilutes the cement gel and raises the effective water-cement ratio in combination of concrete. The workability of the mixtures is directly affected by the increase in water-cement ratio, leading to a higher cone slump value [61]. In Figure 16, the relationship between the concrete CS ($R_c$) and the quantity of RSP is depicted.

The standard deviation of $R_c$ was up to 6%.

The relationship between the quantity of RSP and the change in concrete CS ($R_c$), presented in Figure 16, is well approximated by Equation 9, where *x* is also the RSP content in the mixture.

$$R_c = 56.37 + 0.3275x - 0.06723\,x^2 + 0.001307x^3, R^2 = 0.994 \tag{9}$$

The utilization of RSP as a cement substitute in concrete does not exceed 8%, as evident from Figure 16. At a dosage of 4% RSP there is a slight increase in CS of 0.53%, and at a dosage of 8% the drop in CS is 2.30%. The introduction of RSP more than 8% negatively affects the CS of concrete. Thus, the loss of CS at 12%, 16% and 20% RSP was 5.32%, 12.45% and 17.38%, respectively. The preservation of strength characteristics at the level of the control composition with the introduction of RSP no more than 8% can be explained by the fact that RSP in this amount largely acts as a mineral filler. Correct selection of the dosage of mineral filler in the form of RSP can improve the structure of the concrete composite, making it denser and with fewer open pores [62]. Also, some RSP particles enter into hydration reactions and change the composition of hydration products. Due to the high calcite content in RSP, calcium hydro-carbo-aluminates are formed, which contributes to the formation of the crystalline framework of the cement matrix. However, with the introduction of RSP more than 8%, a negative effect is already observed. Increasing the RSP content increases the effective water-cement ratio and reduces the CSH gel content, and in total, these factors negatively affect the strength of the concrete composite [26]. Concrete's Water-absorbing is shown to be dependent on the amount of RSP that is added, as depicted in Figure 17.

The standard deviation of water-absorbing was up to 5.5%. The dependence of the change in Water-absorbing ($W$) of concrete on the amount of RSP, presented in Figure 17, is well approximated by Equation 10, where $x$ is also the content of RSP in the mixture.

$$W = 5.494 - 0.2068x + 0.02718\,x^2 - 0.000735x^3, \quad R^2 = 0.973 \tag{10}$$

From Figure 17 it can be seen that concretes containing 4% and 8% RSP, introduced to replace part of the cement, have lower Water-absorbing values compared to the control composition and decreased by 6.58% and 7.31%, respectively. As mentioned earlier, the introduction of RSP up to 8% is optimal and reduces water absorption. However, with an increase in the RSP content, a negative effect is already observed. The Water-absorbing of concrete at 12%, 16% and 20% RSP content increased by 5.30%, 10.97% and 16.09%, respectively. The decrease in Water-absorbing of concrete at optimal dosages of RSP is due to the fact that RSP particles act as a mineral filler [63, 64]. Mineral filler particles increase the particle packing density and reduce porosity. The rise in RSP content leads to a decline in CSH gel content, resulting in negative effects. Insufficient CSH gel content causes inadequate lubrication between aggregate particles, resulting in weak adhesion contact zones. In addition to contact zones with weak adhesion of the structural components of a concrete composite, voids can also form, and in total these effects lead to an increase in Water-absorbing and a decrease in the strength of concrete [16].

Regarding the results of assessing the influence of the RSP additive on the properties of concrete, it can be concluded that the selection of the optimal content of this additive makes it possible to maintain the strength properties of the composite at the level of the control composition and reduce water absorption, which is confirmed by other studies. For example, in studies [12, 18, 65], concretes containing finely ground powders obtained from various types of mollusks up to 10% demonstrated good CS and lower permeability. In our study, improvements in physical and mechanical characteristics of up to 10% were also observed in comparison with control samples, which was due to careful preparation of raw materials and the selection of optimal recipe and technological parameters. Thus, the powder from river shells is not inferior to a similar additive from seashells in terms of the properties of the composites containing them.

Optimal percentages of RSP up to 10% for cement mixtures were determined by analyzing the compressive and flexural strength values. Up to 10% RSP, the strength of the hardened cement paste is within or slightly greater than the standard deviation of the strength of the control samples.

Optimal percentages of RSP up to 8% for concrete mixtures were determined by analyzing the water absorption compressive strength values. Up to 8% RSP, the strength of concrete is within the standard deviation of the strength of the control samples or slightly more than it, and water absorption is also within the standard deviation of the water absorption of the control samples or slightly less than it. That is, the results within the specified dosages of RSP can be considered effective, since the characteristics of composites with RSP are not inferior to the characteristics of composites of control samples. Information about this has been added to the text of the manuscript in the "Results and Discussion" section.

The studies carried out yielded a number of important results. It turned out that finely ground river shell powder influences the fundamental nature of the formation of the properties of the resulting new cement composites and their practical applicability as a starting material for the formation of concrete structures [15, 56]. An important aspect was a different picture of structure formation. When forming a concrete mixture, the gel-like component undergoes changes due to the introduction of a new component - powder from river shells. At the physical level, we have the need to reduce the amount of mixing water, since a new component is introduced into the concrete mixture - finely ground powder, which reduces the water requirement of the entire mixture. At the same time, at the chemical level, the combination of concrete is additionally saturated with compounds of calcium bicarbonates, calcium hydro carbo aluminates and calcium hydroxy aluminates. Ultimately, CSH gel, as an ambiguous phenomenon that is of a diverse nature, is complemented in its nature by the micro strengthener of subsequent concrete during the transition from a liquid to a solid state. The role of this micro strengthener is performed by finely ground river shell powder. Additional supply of calcium to the combination of concrete makes it possible to impart completely different properties at the micro- and macro-level to the forming combination of concrete, and subsequently to the concrete structure made from it [57].

In this case, it is necessary to emphasize the special role of prescription factors, namely the optimal dosage of the finely ground river shell powder used. At an optimal level of saturation of cementitious composites, RSP improves their physical characteristics while maintaining strength. At the same time, after the peak of efficiency has been overcome, there is already some oversaturation of the combination of concrete with the modifying powder, which leads to a deterioration in the properties of cement composites. That is, one should understand the dual nature of the action of the new powder in the composition of the combination of concrete [66]. At the stage of formation of the rheological properties of the mixture itself and the formation of CSH gel using a modifier, the chemistry of this process changes significantly. There is a need to reduce mixing water, which makes adjustments to the rheology of the combination of concrete. Ultimately, with the optimal addition of the necessary water, the additional powder does not have a significant effect on the workability of the mixture, and the processes of formation of CSH gel in the composition of such a mixture proceed in accordance with the generally accepted physical and chemical laws of the formation of CSH gels of a conventional combination of concretes [41, 67].

It should be emphasized once again that the positive effect of substituting part of the cement with RSP is possible only with a certain dosage, which must be selected individually for each concrete composition. The number of factors influencing the effectiveness of the physicochemical nature of structure formation with a modifier, the properties of the combination of concrete itself and, finally, the characteristics of concrete, is quite large and varied. These can be recipe-technological factors, as well as external factors, for example, temperature and humidity of the environment, characteristics of the raw materials, the quality of the chemical composition of these raw materials, the absence of any impurities, as well as the reactivity of all components of the combination of concrete [68, 69]. Thus, the authors recommend using the proposed physicochemical effect of structure formation with caution and for each specific case, making a control selection of the composition of the combination of concrete and adjusting the properties of concrete after control tests.

The optimal composition of modified concrete based on RSP, determined by us during the study, takes into account a certain increase in water demand and, in connection with this, the need to adjust the concrete formulation in terms of the water-cement ratio. Refinement of the compositions made it possible to give a rational relationship between the optimal amount of RSP and changes in the water-cement ratio, which made it possible to adjust and minimize the potential risks of changes in workability. All this allows us to recommend the proposed composition of modified concrete for real production.

# 4. Conclusions

The study investigated the impact of river shell powder on cement mixtures and concrete properties. The study determined the properties of fresh and hardened cementitious composites with varying RSP contents:

- The introduction of RSP into the composition of cement mixtures up to 20% instead of part of the cement reduces water consumption and reduces the ST of these pastes. The characteristics of the RSP particles determine the reduction in water demand in cement mixtures. These particles have low reactivity and a dense structure, and a slight reduction in ST at 15% and 20% RSP content is due to the fact that some of the RSP particles that have entered into a hydration reaction will accelerate the process of $C_3A$ hydrolysis.
- The amount of RSP that can be substituted in cement mixtures without compromising their strength properties is limited to no more than 10%.
- The introduction of RSP into a combination of concrete increases the actual water-cement ratio by up to 20% and changes the workability parameters of the combination of concrete, expressed in an increase in cone slump.
- The use of RSP in an amount of up to 8% instead of part of the cement in the concrete composition makes it possible to maintain its strength characteristics at a level comparable to the control composition and reduce Water-absorbing by 7.31%. In optimal quantities, RSP in combination of concrete acts as a mineral filler, due to which the concrete structure becomes denser and physical characteristics are improved.
- The study proposes to continue exploring the formation of concrete structure modified with aquaculture waste, such as shells of dead mussels and river snails.

Proposals for creating a technological line complex in the building materials industry have been proven feasible.

- For the preparation and production of a ready-made modifying additive from crushed river shells,
- As well as the launch of the production of modified combination of concrete and concrete based on the addition of crushed river shells.

The use of recycled calcite-rich river shells can improve the economic and environmental value of cement composites.

# 5. Declarations

## 5.1. Author Contributions

Conceptualization, S.A.S., E.M.S., A.C., D.E., M.K., and N.Q.H.; methodology, S.A.S., E.M.S., and A.N.B.; software, M.K., Y.S., and D.E.; validation, C.A., A.C., S.A.S., E.M.S., and A.N.B.; formal analysis, Y.S., A.C., and C.A.; investigation, N.Q.H., S.A.S., E.M.S., A.N.B., Y.O.Ö., C.A., A.C., D.E., Y.S., and M.K.; resources, A.A.S.; data curation, S.A.S., E.M.S., A.A.S., D.E., M.K., and Y.S.; writing—original draft preparation, S.A.S., E.M.S., and A.N.B.; writing—review and editing, S.A.S., E.M.S., and A.N.B.; visualization, S.A.S., E.M.S., and A.N.B.; supervision, N.Q.H. and Y.O.Ö.; project administration, N.Q.H. and Y.O.Ö.; funding acquisition A.N.B. All authors have read and agreed to the published version of the manuscript.

### 5.2. Data Availability Statement

The data presented in this study are available on request from the corresponding author.

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The authors received no financial support for the research, authorship, and/or publication of this article.

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### 5.5. Conflicts of Interest

The authors declare no conflict of interest.

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