Influence of the physicochemical properties of Portland cement on the strength of reactive powder concrete

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Abstract

The paper presents an analysis of mechanical properties and microstructure of reactive powder concretes RPC manufactured with the use of three different industrial Portland cements diversified in terms of the strength class (42.5 and 52.5), chemical and mineral composition as well as specific surface area. All developed materials were subjected to three different hydrothermal curing conditions. The test results confirm that the factors most influencing the consistency of the concrete mixture are the chemical and mineralogical composition of the binder. However, it appears that when it comes to mechanical properties, the factor which plays the crucial role is the specific surface area of cement. For one of the analysed cements, due to its favourable chemical and mineralogical composition, it was possible to limit the value of W/B ratio up to 0.17, without adversely affecting the properties of the concrete mixture. Nevertheless, it has not contributed to any spectacular increase in strength as compared to materials based on the cement with the largest surface area, where the minimum realizable W/B ratio was 0.20.

Keywords: Reactive Powder Concrete; cement composition; mechanical properties

1. Introduction

Reactive powder concretes, characterized by ultra high mechanical properties, are multi-component cementitious composites, in which the role of the binder is mainly played by cement and silica fume. The average...
volume fraction of this part of composite, also including mixing water and superplasticizer, comprises about 60% of the whole material [1]–[5]. The amount of cement in 1 m³ of concrete mixture ranges from 700 to 950 kg [6]–[8]. Therefore, proper selection of the binder type, i.e. its class, mineralogical and chemical composition and, finally, its specific surface area is very important since it is a factor influencing properties of the concrete mixture and, consequently, of the matured composite. The average values of the water-binder ratio in RPCs are in the range of 0.18 - 0.25 [3], [4], [9]–[11], which in some cases allows obtaining the value of compressive strength exceeding 200 MPa. A parameter associated with consistency of the mixture (in the case of RPC usually expressed in cm as a flow measured on table for mortars [12]), according to [13], should be within very narrow limits of 25 – 30 cm. This is due to two phenomena that may take place during preparation of reactive powder concrete mixtures. The first one is related to the problem of sedimentation of frequently used steel fibres when the flow is greater than 30 cm. The second one is the amount of air entrapped during mixing, reaching even more than 3 – 4 vol.% if the consistency is too thick.

The best results so far, in terms of technological parameters and the subsequent mechanical properties of the matured material, have been achieved with the use of Portland cement CEM I, characterized by strength classes 42.5 and 52.5 [6], [7], [14]. Very few studies are described in [3], [15], [16], in which experimental mixtures were made with the use of cements type CEM II and CEM III. Extensive research on the impact of phase and chemical composition of different cements on the properties of hardened RPC were undertaken by [14]. Three Portland cements of strength class 42.5 and 52.5 were analyzed. They were different in terms of the content of C₃A phase and alkalis as well as the specific surface area. The composites were manufactured preserving constant mass proportions of ingredients, and two different curing regimes were applied during setting (natural conditions at temperature 20°C and steam curing at 90°C). For the cement characterized by strength class 42.5, the best results were obtained using cement CEM I 42.5 LA in both curing conditions (f,c,28(20°C)=188MPa and f,c,28(90°C)=258MPa), whereas the worst when CEM I 42.5 R was applied (f,c,28(20°C)=155MPa and f,c,28(90°C)=231MPa). The reasons for obtaining lower compressive strength in the second case were ascribed by authors [14] to the cement chemical and phase composition, which was characterized by the highest content of C₃A and alkalis as well as surface area. These three parameters were the reason why in order to get sufficiently good rheological properties of the concrete mixture, the amount of mixing water had to be increased from predetermined W/C = 0.23 to 0.25. In the case of cements of strength class 52.5, the compressive strength of all composites after 28 days of setting remained on the same level and varied from 177 to 183 MPa, regardless of the curing conditions or the cement type. However, as in the case of class 42.5, the concrete mixture containing cement CEM I 52.5 R showed the worst workability, although this cement had a smaller surface area than CEM I 52.5 R LA. Thus, [14] concluded that the rheological properties of RPC mixtures are primarily determined by the presence of the C₃A phase and alkaline ions.

In addition to the negative impact of C₃A on rheological properties of concrete mixtures, confirmed several times, consisting in adsorption of superplasticizer molecules on the surface of this phase, [17] gives a number of other reasons for lack of compatibility between cement and superplasticizer. The following factors are mentioned: the form of sulphate ions (i.e. K₂SO₄, Na₂SO₄, anhydrite, hemihydrate, and gypsum) and free calcium oxide. According to the information given in [17], the presence of alkaline ions does not necessarily play a negative role in the process of concrete mixture manufacture. Indeed, the presence of appropriate amounts of Na⁺ and K⁺ supplied in the form of sulphates increases the concentration of SO₄²⁻ in the solution, which leads to more rapid formation of ettringite on the surface of C₃A, and thereby increases the effectiveness of superplasticizer in the mixture. One way or the other, as to the general requirements for selection of proper cement for reactive powder concrete production, authors [8] and [14] agree that it should be characterized by:

- the lowest possible content of C₃A phase,
- reduced amount of alkaline ions,
- relatively low development of specific surface area, so that it would not cause excessive increase in water demand,
- high silica modulus, which provides both excellent rheological and mechanical properties of the matured material.
2. The purpose and scope of research

The first stage of the study was an analysis of the impact of Portland cement type of strength classes 42.5 and 52.5 on the basic properties of the mixture and the mechanical properties of RPC. The tested cements were also diversified in terms of their mineralogical and chemical composition as well as the specific surface development. The reference composition of RPC, where all cements were used consecutively, was established in another research programme and described by [18]. The second stage of the study was to verify the possibility of obtaining the RPC mixture characterized by the lowest possible value of W/B ratio, assuming the appropriate flow and amount of entrapped air, tested in accordance with [12], [19], and, consequently, obtaining a hardened composite with high compressive and flexural strength.

3. Constituents characteristics

Three different industrial Portland cements were selected for the study: CEM I 52.5 R NA; CEM I 42.5 R NA and CEM I 42.5 N MSR NA. Chemical and mineralogical compositions and other basic characteristics are summarized in Table 1. Moreover, the remaining RPC constituents, i.e. silica fume, quartz powder and quartz sand are presented in Table 2. From among several polycarboxylate superplasticizers the one was selected which exhibited the best compatibility with all the tested cements.

| Chemical composition | 52.5 R NA | 42.5 R NA | 42.5 N MSR NA |
|----------------------|----------|----------|--------------|
| SiO₂ [%] | 22.98 | 19.80 | 21.60 |
| CaO [%] | 65.58 | 64.66 | 64.89 |
| MgO [%] | 1.06 | 1.04 | 0.76 |
| Al₂O₃ [%] | 4.41 | 4.97 | 3.44 |
| Fe₂O₃ [%] | 2.10 | 2.79 | 3.50 |
| SO₃ [%] | 3.32 | 2.91 | 2.71 |
| Na₂Oe [%] | 0.51 | 0.48 | 0.32 |
| Cl⁻ [%] | 0.009 | 0.024 | 0.018 |
| Bouge’s phase composition | | | |
| C₃S [%] | 59.1 | 59.8 | 59.6 |
| C₂S [%] | 17.9 | 5.5 | 11.2 |
| C₃A [%] | 8.1 | 8.5 | 3.2 |
| C₄AF [%] | 6.4 | 8.5 | 10.7 |
| Physical properties | | | |
| Required water for standard consistency [%] | 29 | 27 | 26 |
| Initial setting time [min] | 130 | 180 | 225 |
| Final setting [min] | 220 | 235 | 305 |
| Specific area according to Blaine [cm²/g] | 4100 | 3460 | 3160 |
| fc₂ [MPa] | 34.5 | 26.1 | 21.4 |
| fc₂₈ [MPa] | 70.8 | 59.8 | 56.4 |
Table 2. Physicochemical properties of silica fume and micro-aggregate.

| Component       | SiO₂ [%] | Al₂O₃ [%] | Fe₂O₃ [%] | CaO+MgO [%] | Na₂Oe [%] | SO₃ [%] | LOI [%] |
|-----------------|----------|-----------|-----------|-------------|-----------|---------|--------|
| Silica fume     | 95       | -         | -         | -           | -         | -       | 0.7    |
| Quartz powder   | 99.0     | 0.3       | 0.05      | 0.1         | 0.2       | -       | -      |
| Quartz sand     | 98.5     | 0.8       | 0.03      | -           | -         | -       | -      |

Physical properties

| Specific area according to Blaine [cm²/g] | 22.2 | 0.8 | 0.04 |
| Dₘₓ, [μm]                                | 5    | 200 | 500  |
| Density [g/cm³]                          | 2.33 | 2.65 | 2.65 |

4. Concrete compositions

In the first stage of the study the mass ratio of constituents was kept constant, while the type of cement varied (see Table 3). In the second stage of the study, in turn, wherever it was possible, the amount of mixing water was limited to a minimum for each type of cement. The value of W/B ratio was consistently reduced by 0.01, until the accepted limit of flow (about 25cm) and entrapped air (about 4%vol.) were obtained. The proportion between the volume fraction of binder and micro-aggregate Vₜ/Vₐ was constant and equal to 40/60% (see Table 4). Once the new composition for each cement was determined, the tests of mechanical properties were repeated.

Table 3. Reference RPC composition.

| Constituent       | Content [kg/m³] |
|-------------------|-----------------|
| CEM I 52.5 R NA   |                 |
| Cement            | 903             |
| CEM I 42.5 R NA   |                 |
| CEM I 42.5 N MSR NA |           |
| Silica fume       | 181             |
| Quartz powder     | 312             |
| Quartz Sand       | 729             |
| Water             | 217             |
| Superplasticizer  | 18              |
| W/C               | 0.24            |
| W/B = W/(C+SF)    | 0.20            |

5. Experimental set-up

The features adopted for diagnostic purposes were basic mechanical properties: compressive strength and tensile strength at bending. First, a 3-point bending test was carried out, with the constant rate of load 50 N/s. 3 samples of dimensions 40x40x160 mm³ were tested each time. Secondly, in order to determine the compressive strength, 6 cubes – 40x40x40 mm³ in dimensions – were cut out from the broken beams and subjected to loading at the constant rate 2.4 kN/s.
Before the samples were examined, they were subjected to two types of curing conditions most commonly used in RPC technology, i.e. maturing in water and steaming. In order to induce significant changes in the material microstructure, related mainly to the interfacial transition zone between \( \beta \)-quartz and C-S-H phase as well as to the occurrence of crystalline hydrated calcium silicates in the form of tobermorite and xonotlite whiskers, a third group of samples were subjected to high-pressure hydrothermal treatment – autoclaving. All the courses of temperature changes as the function of time during all considered hydrothermal treatments are presented in Figure 1.

- **W** – 28-day setting in water at 20\(^\circ\)C, preceded by 24-hour preliminary setting in a chamber where evaporation of water was prevented.
- **S** – Steaming at 90\(^\circ\)C according to the following cycle: 6-hour preliminary setting in the chamber, raising the temperature to the maximum value for 3 hours, isothermal heating for 12 hours and cooling down to ambient temperature for 3 hours.
- **A** – Autoclaving at 250\(^\circ\)C and pressure 4.0 MPa, according to the following cycle: 24-hour preliminary setting in the chamber, raising the temperature to the maximum value for 7.5 hours, isothermal heating for 12 hours and cooling down to ambient temperature for 7.5 hours.

### Table 4. Modified compositions.

| Constituent       | Reference | 1  | 2  | 3  | 4  |
|-------------------|-----------|----|----|----|----|
| Cement            | 903       | 914| 923| 935| 933|
| Silica fume       | 181       | 183| 185| 187| 187|
| Quartz powder     | 312       | 316| 319| 323| 323|
| Quartz Sand       | 729       | 738| 744| 754| 753|
| Water             | 217       | 209| 201| 191| 190|
| Superplasticizer  | 18        | 18 | 18 | 18 | 21 |
| W/C               | 0.24      | 0.23| 0.22| 0.20| 0.20|
| W/B = W/(C+SF)    | 0.20      | 0.19| 0.18| 0.17| 0.17|

![Fig. 1. Temperature changes in time during the process of steaming (S) and autoclaving (A).](image)
6. Test results

Analysing the concrete mixtures of the composition presented in Table 3, which were prepared with the use of CEM I 52.5 R NA and CEM I 42.5 R NA, we will see that they show similar properties, i.e. the flow about 25 cm and the air content around 4%. It should, however, be noted that the cement of a higher strength class has about 20% greater specific surface. On the other hand, comparing cements of the same strength class, i.e. CEM I 42.5 R NA and CEM I 42.5 N MSR NA, which both have a similar specific surface area, but the MSR variety has limited C₃A (3.2%) and Na₂O (0.32%) content, one can see a significant improvement in the consistency of the mixture – the flow reaches 29 cm, while the entrapped air is limited to 3.9%. This fact confirms that among all the considered factors, the development of cement specific surface has the least influence on the consistency of the concrete mixture. Hence, cement CEM I 42.5 N MSR NA has the greatest potential for further reduction of the water-binder ratio, which is confirmed by the results given in Table 5.

Table 5. Basic properties of concrete mixtures.

| Cement                     | Mix No. acc. to Table 4 | W/B [-] | Flow [cm] | Entrapped air [%] vol. |
|----------------------------|--------------------------|---------|-----------|------------------------|
| CEM I 52.5 R NA Reference* | 0.20                     | 24      | 4.4       |
| CEM I 42.5 R NA Reference  | 0.20                     | 26      | 4.0       |
| 1*                        | 0.19                     | 22      | 4.6       |
| 2                         | 0.18                     | 19      | 5.6       |
| CEM I 42.5 N MSR NA       | 0.20                     | 29      | 3.9       |
| 1                         | 0.19                     | 27      | 3.9       |
| 2                         | 0.18                     | 26      | 4.8       |
| 3                         | 0.17                     | 20      | 5.5       |
| 4*                        | 0.17                     | 24      | 4.5       |

* - composites selected for further mechanical tests

Analysing the results obtained in the tests of the composites mechanical properties, one can conclude that, while the chemical and phase composition of cement play a key role in the mixture consistency, it is the specific surface area that is more important for mechanical properties. As shown in Fig. 2, the composite based on CEM I 52.5 R NA shows the highest compressive and tensile strengths, regardless of the curing conditions.

On the other hand, comparing cements with the same strength class 42.5, we must conclude that they allow creation of RPCs with similar mechanical properties. However, a small strength advantage could be found in the composites made with cement CEM I 42.5 N MSR NA, setting in water and subjected to steaming. Compressive strength is higher by about 6 – 9% and tensile strength at bending by 10 – 20%. The reasons for this improved performance may be traced to both the material and technological factors. First, the phase composition of MSR cement shows a higher total amount of calcium silicates, which release portlandite – Ca(OH)₂ – during hydrolysis, being indeed a substrate for pozzolanic reaction with silica fume. This causes the appearance of greater amounts of the C-S-H phase, thereby sealing the structure of the material. Secondly, it is quite obvious that a greater flow of concrete mixture enables its self-deaeration, as confirmed by the results given in Table 5. Both of the aforementioned reasons bring about a reduction in porosity and, simultaneously, an increase in strength.

The effect of curing conditions on the mechanical properties of RPC is much more evident, especially in the case of high-pressure hydrothermal treatment. Low-pressure curing, i.e. steaming at 90°C for 12 hours, causes an increase by approximately 10 and 20% in compression and tensile strength, respectively, regardless of the used cement. However, the process of autoclaving improves compressive strength by the range of 26 – 36%, but it changes the tensile strength to a much more significant degree. This property, in comparison to setting in water at
20°C, is higher by 60% up to almost 100%, depending on the cement type. Such considerable improvement in mechanical properties results from significant changes in the microstructure, which are described in detail below.

In the second part of the research, consisting in reduction of the mixing water content, in the case of RPC produced with the use of cement CEM I 52.5 N NA, it has been proved impossible to obtain a concrete mixture with a lower W/B ratio, while the flow and the amount of entrapped air remained on the assumed level. On the other hand, as can be seen in Table 5, the composite made with cement CEM I 42.5 R NA shows the potential for reducing the W/B ratio to 0.19, and CEM I 42.5 N MSR NA – up to 0.17. Reduction of the mixing water amount by 0.01, as in the case of CEM I 42.5 R NA, brought about no changes in mechanical properties, but in the case of the MSR cement a slight increase was noted. The compressive and tensile strengths increased by about 4 and 8%, respectively, in all curing conditions.

7. Microstructure

Fig. 3 shows a cross-section of the RPC characterized by the best mechanical properties – the one that was manufactured with CEM I 52.5 R NA. Generally, regardless of the curing conditions, the microstructure of matrix (C-S-H phase) is very tight and compacted in all the composites. The matrix adhesion to inclusion (quartz grain) is reflected in the manner of fracture. In the case of materials cured in water this manner seems to be adhesive, which is confirmed by the traces of C-S-H phase on the surface of inclusion (see Fig. 3A). On the other hand, the composites that were subjected to both steaming and autoclaving show cohesive failure, presented in Fig. 3C by a conchoidal fracture. Additionally, crystalline calcium silicate hydrates in the form of tobermorite and xonotlite appear in the pores of the autoclaved composite, decreasing its micro-porosity (Fig. 3D). This fact is reflected in MIP results presented in Fig. 4.

The influence of W/B ratio in the range from 0.20 to 0.17 on RPC micro-porosity distribution is negligible. In contrast, the factor that causes changes in this characteristic are curing conditions (see Fig. 4). Although the total porosity of steamed RPC and the one cured in water are similar, the autoclaved concrete exhibits clearly reduced porosity in the whole tested range. This has been affected not only by the aforementioned crystals of xonolite and tobermorite filling voids in the material, but also by an increase in pozzolanic reactivity of all RPC components.

To summarize, positive changes in mechanical properties of RPCs subjected to curing at elevated temperatures result from microstructure modification consisting in: i) increasing the reactivity of RPC components and thus filling the empty spaces in the material – mainly by amorphous but also crystalline hydrated calcium silicates, ii) changing the nature of the interfacial transition zone between the matrix and the inclusions, i.e. the C-S-H phase and β-quartz, iii) reducing the total micro-porosity by about 20% as a result of the autoclaving process.
8. Conclusions

In order to obtain reactive powder concretes with adequate mixture properties, the binder used should be characterized by a limited content of C₃A and Na₂O. Highly developed specific surface area of cement (above 4000 cm²/g, according to Blaine), despite the obvious increased water demand, allows obtaining the proper consistency of RPC mixture and, at the same time, its best mechanical properties. Reduction of W/B ratio by 0.03 in RPC based on CEM I 42.5 N MSR NA did not result in significant changes in mechanical properties. The reason for this may be, on the one hand, a slightly reduced capillary porosity, but on the other hand, an increased total porosity caused by enhanced aeration of the concrete mixture. It turned out that of the two analysed technological factors, i.e. the value of W/B ratio and the curing conditions, hydrothermal treatment is the one that affects the RPC microstructure and strength much more intensively.

![Microstructure of RPC cured in different conditions](image)

Fig. 3. Microstructure of RPC cured in different conditions A) in water at 20°C, B) steamed at 90°C, C) and D) autoclaved at 250°C.
Fig. 4. RPC pore distribution in the considered curing regimes.

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