Characterization of fillers made of natural stones as a cement substitute

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Abstract. The article deals with the classification of fillers according to the type and method of rock processing and their use as a partial cement replacement in the concrete mixture. The aim is to better classify fillers by their origin, maximise their usability and design a concrete mixture with effective use of filler as a cement replacement. The article compares the fillers that originated from natural stone. The research is focused primarily on the granite filler, as it is not currently explored in detail. As the results of existing research differ, tests of the filler and its effect on the compressive strength of cement composites were performed, for better characterization of the effect of filler pozzolanic activity. The results of the tests are compared with each other, and the probable causes of differences in the individual research results are described.

1. Introduction

Nowadays, many types of filler are being researched. The primary reason is the saving cement in composites which reduces the price and energy demands of concrete production. Many of the fillers are also secondary or waste materials. Their processing eliminates the problem of landfill. In general, fillers act in cementitious composites as inert addition. They are considered to be chemically inactive and are added to the concrete mixture primarily to improve processability, increase the proportion of fine cement matrix, change the colour of the composite, and the like [1]. Research shows that fillers can have a positive impact on other properties of hardened composites – for example, permeability, porosity, and strength characteristics. The final composite characteristics are highly dependent on the filler used. There exist many research studies on seemingly the same fillers that disprove each other. Therefore, the detailed characteristics of the filler is an essential part of such research (composite design). In addition to the essential characteristics required by EN 12620 + A1 such as bulk density, grain size, chloride, sulphate content, filler purity [2], detailed chemical analysis or mineralogical composition, grain shape, specific surface area and the like are needed, since all these characteristics are dependent on the type of filler.

The primary classification of fillers depends on the origin of the material. These can be human-made materials (brick, ceramic, concrete recycled materials [3]) or natural raw materials. This article describes fillers formed from natural raw materials – rocks. Fillers can be divided according to the types of rocks from which they originate, which has a significant effect on their characteristics. Fillers can also be divided into several groups, according to the methods of their formation. Initial formation where the filler is the desired product and is produced by micronising. Secondary, when the filler is produced as a waste (secondary) raw material. The secondary filler can be further subdivided, for example, according to the method of rock processing. The rock can be crushed into aggregates which creates dust.
The rock can be processed and treated underwater to form a decorative stone. This process produces sludge which must be dried. Those examples show that there are a large number of filler types. Each has specific characteristics and hence different influence in cement composites.

Most of the filler arises probably when the rock is worked on decorative stone. According to some research, up to 58% of the extracted rock is wasted, of which 18% is waste (sludge) resulting from polishing [4]. This value is very individual as it depends on the method of rock extraction and the final product. At the same time, however, it shows how much total waste can be generated. Other research shows that the amount of sludge produced by cutting blocks ranges from 20 to 30% of the rock volume [5]. The documents suggest that the extraction and especially the modifying of decorative stone blocks generate large quantities of fine dust. The problem with landfilling of these wastes is related to it.

In the article, firstly, fillers from fundamental rocks are compared. As many types of fillers may be formed, the article deals in more detail only with granite sludge resulting from wet stone processing (cutting, grinding, polishing). This material was chosen because it has not yet been examined in more detail as other fillers such as marble or limestone. The researches of the effect of the granite dust on cement composite that has been carried out are often contradictory. The article, therefore, draws attention to characteristics and the more detailed classification of fillers, which has a significant effect on the cement composite.

2. Materials and methods
Marble and granite dust was included among the studied materials as they are the most common rocks used as a decorative stone. Furthermore, limestone flour, which is most often used in self-compacting concretes, was compared. Other fillers were chosen concerning aggregate mining in the Czech Republic – gneiss, amphibolite. In this study, the characterization of granite and amphibolite dust have been performed, and the results were compared with other studies focused on marble, gneiss and limestone dust [4, 7–17].

2.1. Grain curve
The essential physical property of each aggregate, the grain size curve is usually measured on sifting systems. According to European standards, the grain filler test should be carried out as with aggregate by screening with an air jet (airflow) (ČSN EN 933-10) [2]. The ideal solution for the determination of the granularity curve, as was done here for granite dust, is the laser diffraction method, which gives more accurate and detailed values. Also, essential statistical data such as modus, median, arithmetic grain diameter or standard deviation can be determined.

2.2. Specific surface
At first, a specific gravity test was performed using a pycnometer. Depending on this value, other material properties such as specific surface area can be calculated. A separate test of the specific surface was carried out by permeable method using Blain apparatus.

2.3. Shape of grains
The shape of the grains is a significant feature for use in cement composites. This test is not always carried out, but the shape of the filler grains has a significant effect on the fresh mixture (rheology, processing) as well as on the hardened composite. The tests were carried out using software on electron microscope images. In the paper, granite and amphibolite dust were examined using the software. The tests were performed on more than ten samples, and the number of particles tested was always given. Circle equivalent diameter, Aspect ratio and Circularity were measured. The circularity can range from 0 to 1, with a perfect circular shape having a value of 1 and elongated shapes having values close to 0.
2.4. Chemical analysis
The EDS (Energy Dispersive Spectroscopy) analysis was performed on the samples. Multiple samples from each rock were tested, and a more significant amount of grain (area) had to be measured. In the case of smaller focus and larger grain, the analysis was biased. The measured values were compared with those of other researches from India, China, and others. This method is comprehensive, so there is a wide range of results suitable for comparison.

2.5. Measurement of pozzolanic activity
The test of pozzolanic activity may be direct and indirect. Both were used in this research. This measurement is customary for chemically active admixtures in concrete, such as fly ash, metakaolin or micro silica. As the filler is only considered as an inert material, this test (direct pozzolanic activity in particular) is not typically performed. For comparison of individual fillers, it is advisable to include the exam in the research. It shows the chemical activity of fillers, possibilities of use and suitability for use in cement composites.

2.5.1. Direct pozzolanic activity.
There are several types of tests. A modified Chapelle test was used for this purpose. The method is based on the pozzolanic ability to combine with CaO. The Chapelle test result is expressed as the amount of Ca(OH)$_2$ in mg bound to 1 g of pozzolan. A material is considered pozzolanic if the test result is at least 650 mg Ca(OH)$_2$ g$^{-1}$ [3, 6]. Tests were carried out on dust from the quarries in the Czech Republic (amphibolite), granite sludge and its heat treatment at 800°C with a duration of 2 hours. For marble and limestone, this test makes no sense since they do not contain SiO$_2$.

2.5.2. Indirect pozzolanic activity.
From these methods, the modified Strength Activity Index (SAI) for fly ash and micro silica, the activity index, was selected. The tests are based on the standards ČSN EN 450-1 (722064) Fly ash for concrete. Part 1 and EN 13263-1 + A1 (722095) Silica fume for concrete. Part 1. According to standards, three mortar mixtures with standard quartz sand have been designed for cement strength tests. In the first case, a reference sample with only standard sand and CEM I 42.5 cement was designed. In the second case, a mixture was designed according to the standard for the specified efficiency index for fly ash, and the cement replacement weight was 25% granite dust. The third mixture was designed according to the silica fume standard, and the investigated filler replaced 10% cement weight. Strength tests were carried out after 3 and 28 days on prisms 40/40/160 mm and cubes 40/40/40 mm.

3. Results
The tests we conducted were partially compared with results from other studies. Among the first characteristics is the grain curve, respectively, the maximum grain of the filler. Some literature reports only the maximum grain (sieve passage). These values are most often given as 0.125 mm; 0.100 mm; 0.075 mm; 0.063 mm; 0.060 mm. Others report the average aggregate grain. The most suitable expression is through a grain curve or particle size distribution which is expressed numerically (e.g. D10, D25, D50, D75, D90). In particular, the D10, D50 and D90 values are published in the papers.
Table 1. A particle size distribution in μm.

| filler | citation | D10 | D25  | D50  | D75  | D90  |
|--------|----------|-----|------|------|------|------|
| granite | [7]      | 1.901 | 5.002 | 13.202 | 28.83 | 51.946 |
| granite | [8]      | 1.105 | 3.500 | 10.000 | 20.000 | 30.000 |
| granite | [9]      | 0.840 | 3.480 | 13.340 | 26.680 | 40.000 |
| granitea | [9]      | 0.840 | 3.480 | 13.340 | 26.680 | 40.000 |
| granite | [10]     | 3.700 | 21.400 | 67.000 |      |      |
| gneiss | [11]     | 3.461 | 22.825 | 86.668 |      |      |
| gneiss | [11]     | 2.864 | 18.902 | 66.811 |      |      |
| amphiboliteb | [12] | 5.661 | 54.445 | 204.691 |      |      |
| limestoneb | [12] | 3.435 | 43.247 | 147.624 |      |      |
| marbleb | [13]     | 2.300 | 33.000 | 350.000 |      |      |

a filler was produced by micronising
b values were subtracted from the graph

For example, if only the maximum aggregate grain is given, it is advisable to supplement the results with another characteristic. In this case, a specific surface can be used. It can also be compared with a cement value, which is approximately known or recorded in the technical datasheet. At the same time, this comparison suggests the suitability of using a filler. According to researches, the specific surface area of fillers is in the range of 300–450 m²kg⁻¹. There are also smaller values of about 240 m²kg⁻¹ [4, 8, 14], especially for fillers of marble and limestone. According to our research, the specific surface of granite dust is 437 m²kg⁻¹.

Another characteristic is the grain shape. According to the SEM figures in the available literature [15], the granite, marble, limestone and gneiss filler grains are similar, which is also evidenced by the aspect ratio from the article [15]. Granite dust and amphibolite were compared in our research (table 2). A significant difference can be seen from the SEM figures (figure 1). As shown in the figure, the vast majority of amphibolite grains are acicular. Poor grain quality is confirmed by a roundness of 0.527, which is lower than that of granite dust.

Table 2. The grain shape.

| Rock type | Amount of particles tested (pcs) | Circle equivalent diameter (μm) | Aspect ratio (-) | Circularity (-) |
|-----------|--------------------------------|-------------------------------|------------------|-----------------|
| Granite   | 73                             | 28.0                          | 0.623            | 0.641           |
| Amphybolite | 106                           | 23.3                          | 0.533            | 0.527           |

Figure 1. SEM granite dust (left), amphibolite dust (right).
The chemical composition of the filler has a significant influence on its reaction in the cement composite. In Table 3, it can be seen that a significant difference in chemical composition is not only among the filler types but also the same filler from a different quarry. The difference can be observed even in row 1, where all samples are from the same quarry.

Table 3. The chemical composition of the filler.

| filler   | SiO₂  | Al₂O₃ | Fe₂O₃ | Na₂O | K₂O | CaO   | MgO   | LOI  |
|----------|-------|-------|-------|------|-----|-------|-------|------|
| Granite  | 48.6–62.9 | 14.1–14.6 | 6.3–8.0 | 3.0–4.2 | 8.0–9.8 | 2.6–4.5 | 3.5–5.9 |
| Granite  | 53.2–94.2 | 1.3–14.1 | 0.4–12.3 | 1.2–3.6 | 0.1–0.2 | 1.0–9.1 | 1.7–8.3 | 0.3–5.0 |
| [4, 16]  |       |       |       |       |       |       |       |      |
| Granite  | ( ~ 60) | ( ~ 14.0) | -     | ( ~ 3) | -   | ( ~ 2) | -     |
| Amphibolite | 44.82 | 14.51 | 13.46 | 0.49 | 6.38 | 20.33 |
| Gneiss [15] | 70.13 | 15.95 | 0.9  | 0   | 6.22 | 1.12  | 0.69 | 2.77 |
| Marble   | 0.2–14.8 | 0.1–21.9 | 0.1–36.8 | 0.0–9.3 | 0.1–0.2 | 6.0–83.2 | 0.4–9.3 | 2.5–46.0 |
| [4, 13, 16] |       |       |       |       |       |       |       |      |
| Marble   | ( < 1.5) | ( <1.0) | ( <0.5) | ( <1.0) | ( <0.1) | ( ~ 50.0) | ( <0.7) | ( ~ 43.0) |
| Limestone| 0.0–3.3 | 0.3–0.8 | 0.0–0.6 | 0   | 0   | 42.6–92.9 | 0.0–9.6 | 1.2–43.7 |
| [4, 16, 17] |       |       |       |       |       |       |       |      |
| Limestone| ( ~ 0.10) | ( ~ 0.30) | -   | ( < 0.0) | ( < 0.0) | ( ~ 50.0) | ( ~ 1.0) | ( ~ 43.0) |

*a Chemical composition in one quarry

*b Chemical composition from multiple quarries

*c Common (most common) values

The reactivity of the filler is related to its chemical composition. Using the modified Chapelle test, it has been shown (Table 4) that although materials contain large quantities of silicon, they are not very reactive and do not meet the standard requirements. Granite dust is more reactive than amphibolite and by modification (heating) its reactivity can be increased by about 50%. Even then, it does not comply with the standard.

Table 4. Chapelle test.

| sample       | mg Ca(OH)₂ g⁻¹ |
|--------------|----------------|
| Granite      | 345–374        |
| Modified granite | 535           |
| Amphibolite  | 75–150         |

The last test of the filler was an indirect determination of pozzolanic activity. The flexural strength on the mortar prisms three days after concreting reached the highest values for the first mixture, consisting only of sand and cement. After 28 days of concreting, the highest values of flexural strength were measured for mixture with 10% of granite dust as cement replacement (Figure 2).
6

Figure 2. The flexural strength on the mortar prisms.

The highest value in compressive strength three days after concreting was achieved with the 25% cement replacement mixture (figure 3). In tests after 28 days, the highest average compressive strength values were measured with a 10% cement replacement mixture. Since direct tests of pozzolanic activity did not meet the standard requirements, higher compressive strength is likely to be due to denser structure caused by the better filling of cement stone with micro-filler.

Figure 3. Direct pozzolanic activity test – compressive strength.

4. Discussion

Grain size and distribution were solved as a fundamental characteristic. All grains are less than 0.125 mm in both research and literature, except amphibolite. Granite sludge had 90% grains smaller than about 55 μm, except for sludge treated with micronising (13.34 μm). The gneiss and amphibolite (crushed) fillers had larger grains. Significantly larger grains of amphibolite are probably due to their shape, where acicular grains are less likely to fall through the sieves. A positive effect of the filler size is given in a paper [9], where the smaller-grain mortar had higher strength than the larger-grain mortar (table 1). Overall, the mortars in this research had lower strengths than the reference mortar, due to an incorrectly calculated water coefficient. A suitable complement to the grain size is the specific surface, which is not often investigated. The results show that the fillers usually have a similar specific
surface area as the cement, indicating a proper use of filler in cement composites. According to the literature [4, 8, 16], marble and limestone fillers may have a smaller surface area (approx. 240 m²·kg⁻¹) than granite dust. All investigated and compared fillers had a similar aspect ratio except amphibolite, which had a lower circularity than granite dust. For these reasons, amphibolite is not suitable for use in cement composites as it worsens their rheology.

In the chemical composition (table 3) the substantial differences can be seen not only between the kinds of fillers but also within a single filler. This characteristic is influenced by the location of the quarry and the homogeneity of the rock. Even in a single quarry, there can be a change in chemical composition during mining. In table 3, common chemical composition values that occur most often are written in brackets. In granite, gneiss and amphibolite fillers, the predominant component was silicon oxides (SiO₂) and aluminium oxides (Al₂O₃). Conversely, marble and limestone fillers contained 50% calcium oxide (CaO), and a large part consists of loss on ignition (LOI). The direct pozzolanic activity was measured for granite dust and amphibolite as they contain a large amount of silicon. The results confirmed that there is insufficient activity according to the standard (650 mg Ca(OH)₂·g⁻¹) and therefore it is not mostly amorphous silicon. Granite dust demonstrates significantly better values than amphibolite, and by heat treatment, the pozzolanic activity can be increased by 50% to 535 mg of Ca(OH)₂·g⁻¹. Still, it does not meet the standard value. On the contrary, the indirect test of pozzolanic activity was positive according to the standard. The efficiency index after 28 days was 110.26% for a 10% cement replacement. It thus meets the criterion of the standard (ČSN EN 13263:1 + A1) according to which it was tested. Positive results were also achieved by the second applied standards (EN 450-1) when the efficiency index exceeded the required value of 75% by 11.43%. Since the direct pozzolanic test was negative, the better strength characteristics are probably due to the denser structure of the composite. These results are also confirmed by a paper [17], where the strength increases with the bulk density of the composite. According to the comparison of available papers, it is clear that the water coefficient has a significant influence on the resulting characteristics of the composite. In cases where the water coefficient was calculated precisely (water weight/cement weight), the strength characteristics were better with the granite filler. In contrast, when calculating the water coefficient, including the filler weight, the strength characteristics of the granite dust composite were smaller than the reference composite. Even so, the research [16] considered the water coefficient including partly the granite filler in its cement ratio, the strength characteristics of some recipes were still slightly positive.

5. Conclusions
Granite dust has approximately the same grain size. Compared to the fillers produced by crushing (gneiss, amphibolite), it has smaller grains. The grain size affects the strength characteristics of the cement composites. It is essential to test the specific surface, which is not often tested. The specific surface of the fillers is similar to that of cement. Limestones and marbles may have a smaller specific surface. Grains of granite, gneiss, marble, limestone filler are more suitable for use in concrete composites than amphibolite filler. Its grains are predominantly elongated and have an acicular shape. Therefore, amphibolite is not suitable due to the processability of the mixture.

The chemical composition varies for both multi-quarry fillers and within a single quarry and has a significant effect on reactions in concrete. Granite, gneiss, and amphibolite fillers can be expected to have a partial pozzolanic reaction as they contain a large amount of SiO₂. According to the direct pozzolanic activity test, any filler does not meet the standard values for pozzolan. Granite dust has higher pozzolanic activity than amphibolite. At the same time, granite dust can be partially activated by heat treatment. The indirect method showed a positive effect of granite dust on strength characteristics of cement composites. As the direct test result of pozzolanic activity was negative, the better strength characteristics are due to the denser structure of the cement composite. An essential condition is the correct calculation of the water-cement ratio, which is a common problem in other researches, and the strength of the filler mortars is lower than the reference mortars.
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