The effect of various pozzolanic additives on the concrete strength index

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Abstract. The concrete industry is searching continuously for new effective mineral additives to improve the concrete properties. Replacing cement with the pozzolanic additives in most cases has resulted not only in positive impact on the environment but also has improved strength and durability of the concrete. Effective pozzolanic additives can be obtained from natural resources such as volcanic ashes, kaolin and other sediments as well as from different production industries that create various by-products with high pozzolanic reactivity. Current research deals with effectiveness evaluation of various mineral additives/ wastes, such as coal combustion bottom ash, barley bottom ash, waste glass and metakaolin containing waste as well as calcined illite clays as supplementary cementitious materials, to be used in concrete production as partial cement replacement. Most of the examined materials are used as waste stream materials with potential reactive effect on the concrete. Milling time and fineness of the tested supplementary material has been evaluated and effectiveness was detected. Results indicate that fineness of the tested materials has crucial effect on the concrete compressive strength index. Not in all cases the prolonged milling time can increase fineness and reactivity of the supplementary materials; however the optimal milling time and fineness of the pozzolanic additives increased the strength index of concrete up to 1.16 comparing to reference, even in cases when cement was substituted by 20 w%.

1. Introduction
Traditionally the most common pozzolanic materials are metakaolin, fly ashes, natural pozzolans and silica fume. Extensive research on these materials has been performed and the results published in the scientific literature [1], [2]. It was detected that only two important parameters should be determined when micro and nano additives are used in cement or concrete [1]. First is the size effect based on the particle nature; it can be used as filler. The second important effect is the pozzolanic activity of the cluster compounds. In the scientific literature no systematically collected information has been available about the industrial by-products which could be used in concrete industry as micro- or nanofillers, having pozzolanic properties without thermal or mechanical treatment. Potential raw materials and treatment processes should be tested to evaluate activity and effectiveness of the obtained micro-filler materials in the concrete industry.
In the developed countries the rise of industrial production is often accompanied with the increase of by-products and industrial waste. For this reason researchers are looking for new technologies of waste processing which would allow to use as new materials in production of the building materials and products, thus developing a waste free production technology [3]–[5]. There are the by-products which are hazardous if disposed in the environment, i.e. lead containing waste glass cullets are not suitable for traditional recycling due to their chemical composition. However, such materials could be ground to powder-like particles and disposed as microfiller in the concrete to improve its mechanical and physical properties [6]. Glass powder has proved to be effective as micro-filler material in the ultra-high performance fibre reinforced concrete [7]. The finely ground coal bottom or grass ashes possess pozzolanic properties and its effective disposal in the concrete has been proven [8]–[10]. Due to pozzolanic and microfilling effects of these particular mineral admixtures, they are capable of enhancing the durability through pore refinement and reduction in the calcium hydroxide of the cement paste matrix [11]. Despite several investigations available about the usage of waste materials in the concrete industry, there is no fast and precise method of how to predict the potential of waste material usage according to its mineralogical, chemical or physical properties. A number of studies have reported that pozzolanic activity depends basically on three factors: the content of amorphous silica, the particle specific surface area and the particle size distribution [12]. Consequently it can be concluded that efficiency of the material usage in the concrete industry can be increased by only applying simple waste product pre-treatment methods.

Several methods are developed to determine pozzolanic activity [14]. Main difference among these methods is the speed, simplicity and precision of the respective method and the reliability of obtained results. The most common method to determine pozzolanic reactivity of the material is to evaluate in time scale reaction processes in cement and pozzolanic material paste. During the cement hydration and other reactions the free portlandite reacts with pozzolans reducing the amount of lime in the paste. This method is common for commercial pozzolans, such as silica fume, where pozzolanic reaction rate and intensity is predictable [15]. The result interpretation in the cement-pozzolana systems is complicated, if the pozzolanic material is made from waste materials. Although high pozzolanic activity is an advantage of the additive used in concrete, it will not always lead to the increased durability of concrete due to chemical corrosion caused by other impurities in the additive. The organic content and alkali content are the most common impurities that can decrease the concrete sustainability. If the additive has low pozzolanic activity, it can still be efficiently incorporated into the structure of concrete thus contributing to higher strength and durability. Compared to some traditional microfillers, such as limestone, the drawback could be the reduction of technological properties, such as workability of concrete [13].

In the present research the pozzolanic material testing methods, such as the specific surface area, the particle size distribution and the pozzolanic activity, were analyzed for various industrial by-products used as microfillers with pozzolanic properties in the concrete, and their efficiency was evaluated with help of the calculated concrete strength index.

2. Materials and Methods
The coal combustion bottom ash (CCBA), the commercial illite clay bricks (CB), the barley ashes (BA), the waste glass (WG), the waste metakaolin (MK) and the illite (IC) clay calcined at laboratory furnace were examined as the supplementary cementitious materials in concrete mixture composition. Selected materials were pre-treated to obtain powder like material in order to make these materials suitable for adding as partial cement replacement in the concrete. Before their testing and adding in the concrete mixtures, these materials were prepared by using thermal or mechanical treatment. Depending on origin of the materials, they were ground in the planetary ball mill Retch PM400 with 300 rpm (CCBA, BA, WG) for different periods of time (i) and were subject to thermal treatment at different temperatures as well as to grinding (IC, MK) (ii). The mixture compositions and testing conditions of the described
samples are given in the references and mechanical tests were performed according to LVS EN 12390-3.

Morphology of the materials was determined with scanning electron microscope (SEM) TESCAN Mira/LMU Field-Emission-Gun. The specific surface area was determined with BET nitrogen absorption porosimeter Nova 1200 E-Series, Quantachrome Instruments. Particle size distribution was detected with Zeta potential “90 Plus” and “MAS ZetaPALS Brookhaven Instr” (with limit from 2 nm to 3 µm).

Pozzolanic activity of the supplementary cementitious materials was determined by the thermogravimetric analysis and the Frattini test. To determine pozzolanic activity by the mass method, 1 g of pozzolanic material is diluted in 100 ml of filtrated lime solution and mixed in the magnetic mixer for 3 h and then filtrated. 25 ml of the obtained solution was added to 50 ml of distilled water and 5 drops of 1 % phenolphthalein was used as indicator. Titration was done with 0.1M HCl solution until its color changed. For reference purposes the lime solution was titrated. The activity is determined as reacted CaO content (reduction). In the concentrated HCl soluble R₂O₅ (Al₂O₃+Fe₂O₃+ TiO₂) the measurements are related to the oxide content in pozzolanic material which has reacted with lime and therefore could be used to evaluate pozzolanic activity.

3. Results and Discussion
The shape of particles was analysed with SEM and their rectangularity was described, i.e. waste glass (WG) and barley ashes (BA) have irregular shape but waste metakaolin (MK) or calcined illite clay (IC) have plate-like structure. SEM images allow to describe homogeneity, size and shape that dominate in the additive (Figure 1).
Figure 1. Micrograph of pozzolanic material: a) metakaolin (MK); b) calcined illite clay (IC); c) waste glass (WG); d) coal combustion bottom ash (CCBA); e) barley ash (BA).

The content of active $R_2O_3 (Al_2O_3 + Fe_2O_3 + TiO_2)$ increases from 6.0 to 32.7 w% for waste metakaolin (MK) and from 5.4 to 7.8 w% for calcined illite clay (IC) after rising calcination temperature of clay from 500 to 800 °C. Active SiO$_2$ increased to 1.2 w% by rising temperature to 800 °C. The surface area of calcined clay did not increase by extending the grinding time, i.e. surface area for 15 min ground IC was 21.95 m$^2$/g and for MK – 16.52 m$^2$/g, for 20 min ground IC was 22.17 m$^2$/g and for MK – 19.42 m$^2$/g, but for 30 min ground IC – 21.40 m$^2$/g and for MK – 15.86 m$^2$/g. Therefore it is not useful to grind calcined clays for prolonged period of time. IC and MK (calcined at 700 °C and ground for 20 and 30 min) were used as cement replacement, adding them up to 20 w% of cement.

The compressive strength of the concrete which is made with calcined and ground clays after 28 days is given in Figure 2. The results indicate that MK ground for 20 min (MK20) increases the compressive strength of concrete up to 86 MPa (strength index 1.16), while 30 min ground MK (MK30) – 82 MPa (strength index 1.11). Compressive strength of the concrete made with 20 min ground IC was 72 MPa and with 30 min ground IC – 74 MPa (strength index 0.97 and 1.00) respectively, compared to the reference concrete (REF) strength 74 MPa (strength index 1.00). Higher active $R_2O_3$ content, which was detected in MK, provided higher strength gain of concrete while prolonged grinding proved to be less effective.

Figure 2. Concrete strength index of 28 days old concrete where 20 w% of cement had been replaced with kaolin clay calcined at 700 °C and ground for 20 min (MK20) and 30 min (MK30) and with illite clay calcined at 700 °C and ground for 20 min (IC20) and 30 min (IC30), REF-reference [16].

The recycled illite clay demolition bricks (CB) were tested as additive in the concrete. In the concrete mixtures the cement was partially replaced with the CB in amount of 20 w%. After the end of building
life cycle, the commercial bricks (CB) can be ground until particle surface area reaches 21.37 m²/g. The content of active SiO₂ was 0.2 w% and R₂O₃ – 1.0 w%. The low content of active compounds compared with the illite clay IC calcined at the laboratory furnace could be explained by calcination temperature during brick production (from 1035 to 1040 °C), which could promote decomposition of amorphous compounds and appearing of crystalline phases.

The compressive strength of the concrete with CB additive is given in Figure 3. The concrete strength index of the concrete with CB additive continuously increased and after 28 day curing was 0.95 of reference (77 MPa) and at the age of 60 days – 0.98 of reference (79 MPa).

![Figure 3. Concrete strength index of concrete where 20 w% of cement had been replaced with the ground commercial bricks additive (CB) [17].](image)

Increase of the coal combustion bottom ash (CCBA) grinding time from 4 to 15 min has increased the specific surface from 1.20 m²/g to 9.60 m²/g, however prolonged grinding period (up to 45 min) has increased the surface area only to 9.85 m²/g.

The amount of active SiO₂ + R₂O₃ does not rise significantly by increasing the grinding time from 4 to 30 min – from 6.35 w% to 7.37 w%. The particle size distribution of the ground CCBA is given in Figure 4. As to the CCBA ground for 4 mins, only 11.3 % of particles were finer than 125 μm, but their amount increased significantly by extending the grinding period. Comparing the particle size distribution of the CCBA ground for 15 and 30 min, the amount of fine particles (<125 μm) rises from 47 to 51 %, which is insignificant gain. By extending the grinding period to 45 min, the amount of particles which are finer than 125 μm reaches 75 %.

In the concrete mixtures the cement was partially replaced with the 4 and 15 min ground CCBA in amount of 20% and 40%. Compressive strength of concrete was tested for 7, 14, 28 days old specimens to determine the pozzolanic effect of CCBA (Figure 5). It was observed that the mixes where cement was partly replaced with CCBA have lower compressive strength after 28 days compared to the reference specimens (47 MPa). The strength index was in range from 0.57 to 0.66 for 40 w% cement replacement and from 0.91 to 0.96 for 20 w% cement replacement. The CCBA with grinding period of 4 min showed compressive strength 45 MPa but the CCBA with grinding period of 30 min showed compressive strength 43 MPa. Difference between these specimens was only 2 –4 MPa, which is not significant. It was observed that among the specimens where cement has been partly replaced, the specimens with 40 w% cement replacement have significantly lower compressive strength results.
Figure 4. The effect of grinding time on particle size distribution of coal combustion bottom ash [18].

Figure 5. Concrete strength index of the concrete mixtures with coal combustion bottom ash (CCBA): REF – reference, CCBA4/20 – 20 w% replacement of cement by the CCBA ground for 4 min, CCBA4/40 – 40 w% replacement of cement by the CCBA ground for 4 min, CCBA15/20 – 20 w% replacement of cement by the CCBA ground for 15 min, CCBA15/40 – 40 w% replacement of cement by CCBA ground for 15 min [9]. [18].

The barley bottom ash (BA) used in research was taken from various local heating plant furnaces in Latvia. To obtain material with homogenous composition, barley bottom ash was ground in laboratory ball mill for 4 and 8 min. The specific surface area of the barley ash ground for 4 min was 0.41 m²/g but for the 8 min ground – 0.47 m²/g. The active SiO₂ was 0.6 w% and R₂O₃ – 2.6 w% for both samples. In the concrete mixtures the cement was partially replaced with the 4 and 8 min ground barley ashes in amount of 20 and 40 w%. The compressive strength results are given in Figure 6.

The reference samples provided the highest compressive strength after 7 and 28 days, 35 MPa and 41 MPa respectively. The samples with the 4 or 8 min ground barley bottom ash replacing 20 w% of cement (4/20 and 8/20) after 28 days curing provided compressive strength 30 MPa and 31 MPa respectively (concrete strength index 0.73 and 0.76). Compressive strength for concrete samples where 40 w% of cement was replaced with the 4 and 8 min ground ashes was the lowest among these mixes. Their compressive strength after 28 day hardening period was 23 MPa and 25 MPa (concrete strength index 0.56 and 0.61).
Figure 6. Concrete strength index of the concrete mixtures with ground barley ashes (BA): REF reference, 4/20 – 20 w% replacement of cement by the BA ground for 4 min, 4/40 – 40 w% replacement of cement by the BA ground for 4 min, 8/20 – 20 w% replacement of cement by the BA ground for 4 min, 4/40 – 40 w% replacement of cement by the BA ground for 8 min, 8/40 – 40 w% replacement of cement by the BA ground for 8 min [9].

The waste glass obtained from fluorescent lamp recycling centre was ground in planetary mills for 30 and 60 min resulting in powder-like material. Active SiO\textsubscript{2} was 0.5 w% and R\textsubscript{2}O\textsubscript{3} – 0.4 w% The particle size of industrially ground glass powder was in range from 6 to 70 µm and the surface area was 0.25 m\textsuperscript{2}/g. The surface area of glass particles additionally ground in planetary ball mill for 30 min increased to 0.63 m\textsuperscript{2}/g. Prolonged grinding time (60 min) resulted in increased surface area of particles to 1.68 m\textsuperscript{2}/g and the particle size was detected in the range from 0.3 to 10 µm.

The compressive strength of the concrete made with ground glass additives (replaced 20 w% of cement in the composition) was influenced by fineness of the glass particles (Figure 7). The compressive strength of concrete rose from 56 to 65 MPa (at the age of 84 days) by increase of glass fineness (strength index from 0.94 to 1.08). The concrete strength index was higher at an early age for the concrete with glass additive (up to 1.20), while the strength index decreased during curing, which might indicate harmful reaction inside the concrete structure.

Figure 7. Concrete strength index of the concrete where 20 w% of cement had been replaced with ground waste glass: S0 - industrially ground glass powder, S30 - 30 min ground waste glass, S60 - 60 min ground waste glass [6].

4. Conclusions
The following conclusions have been drawn from this study:
1. Proper pre-processing conditions of the waste materials and by-products, such as temperature treatment and grinding time, can lead to secondary raw mineral filler or even pozzolanic materials suitable for application in the concrete industry.
2. The effectiveness of the secondary raw materials depends on origin and nature of these materials, while proper pre-treatment could increase the concrete strength index up to 1.16 comparing to reference, if up to 20 w% of cement are replaced.

3. The cement replacement by 40 w% will result in high strength index decrease of concrete at early age (from 0.43 to 0.51), while prolonged curing is followed by the concrete strength increase up to 0.56 to 0.66 of reference.

4. Prolonged milling time is not always advisable for specific type of additive (such as clay) and can reduce the obtained material environmental and technological efficiency in application.

5. In some cases the increase of specific surface area by grinding also increase amount of active R₂O₃/SiO₂ and waste stream additive pozzolanic activity thus significantly improving the concrete strength index.

6. Fine grained waste stream mineral materials with high active R₂O₃/SiO₂ and low organic and alkali content can be considered as potentially effective additive material in concrete.

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