Research of cement mixtures with additions of industrial by-products

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Abstract. The main goal of the article is the comparison of the possible use of secondary energy products. Used fly ashes, respectively steel dusts in cement mixes derive from production in Moravian-Silesian Region. The research focused on their influence on the chemical and physico-mechanical characteristics of the fresh and solid mixture. The aim was to find suitable formulations for grouting works, highway construction possibly rehabilitation of underground cavities created by mining activities. The introduction is mentioned the history of waste utilization up to current use as a product and the overall state of the problem. The conclusion is an evaluation of possible use in practice, including recommendations to carry out further tests.

1. Introduction

In the Czech Republic, the production of fossil fuels (especially brown coal) has the highest part of total production. In the heating plants and power plants is burned mainly brown coal extracted in underground or open pit mines in northwest and northeast parts of Czech Republic. This involves with high production of solid residues after combustion or accompanying products from desulphurization. The forming of dumps, where is stock-pilled industrial waste arising from the diversified industrial processes, is a common fact. There are several dumps in the Czech Republic. Nowadays, these products, not dangerous waste as in past, can further be used because of their positive properties. The fly ash has more or less distinctive puzzolanic properties in depending on his contents. These properties make fly ash suitable material for construction purposes. Use of this material would become a solution to the required reduction of natural resources extractions such as aggregate and limestone.

For their use, for example as solid backfill material is important to verify their properties to meet all standard requirements. A large scale of secondary materials is being tested today to improve the resulting product properties. And one such example is the use of organic waste as filler in the production of mortar [1, 2, 3, 4] Another such example is a similar issue, the use of waste recycled complementary product on a natural basis into building materials, was dealt with in an article entitled "Implementation of waste cellulosic fibers into building materials [5, 6]. Research on this topic is deal with research of Concrete Containing Recycled Concrete Aggregate with Modified Surface in combination with the efficient use of resources and the achievement of the material properties of the resulting of these composite’s [7, 8].
2. Description of mortar components and their properties

2.1. Cement fine
It is a mixture of mineral filler with a grain size 0 - 0.7 mm, portland cement and additives that improve processing and use properties of the product. Cement is most common used hydraulic binder.

2.2. Fly ash
Fly ash is material incipient by the combustion of extracted coal for the purpose of electric production in power plants. The fly ash has more or less distinctive puzzolanic properties in depending on his contents. These properties make fly ash suitable material for construction purposes. Ash properties depends primarily on the type of combustion coal, grain size and combustion conditions, as well as on the chemical and mineralogical composition of used fuel. Physically, fly ash is a light brown to dark gray, very fine dust with a particle size 1 to 400 microns, with glassy structure and in most cases with rounded grain shapes resulting from steep cooling during the combustion process. The chemical composition of the fly ash consists primarily of silicon, aluminum, calcium, iron, magnesium, sulfur and alkaline oxides, as well as residues of combustible materials. In more detailed description of fly ashes, emphasis is placed on two of his properties that greatly influence its usability: the content of active puzzolanic SiO2 and CaO and the grain size. It has been found, that a at smaller grain size of fly ash (25 microns) is positively affected its puzzolanic characteristic, therefore these fine fractions are preferred over the coarse fraction. According to puzzolan activity of fly ash is determined ability to produce a solid mixture in the presence of CaO. Puzzolanic activity also could be directly affected by aluminium content, grain size, loss by ignition or alkali content (Na2O). Granular fly ash: These kind of fly ash is made by “classic” fuel combustion process at a temperature about 1400 to 1600 °C. They are distinguished mainly by β-quartz and mullite (3Al2O3·2SiO2) together with a glassy phase in an amount usually greater than 50 %, which in essential way under normal or higher temperatures contributes to the reactivity of fly ash with CaO or cement. Under hydrothermal conditions mullite in low extents also enter into reaction. Fluid fly ash: Some types of power plants or heating plants use fluidized combustion technology at atmospheric pressure. Ground fuel with the addition of limestone or dolomite is burned in the circulating layer at 860 °C. During the disintegration process, from fuel is released SO2 and is bound to CaSO4. This is particularly important from an ecological point of view, because otherwise sulphur dioxide leak into the atmosphere, resulting in very harmful acid rains. These improved processes, thanks to transported burnt gas from furnace area, lead to separation of individual fractions, fine parts in form of flue dust are carried away and coarse parts remain in the combustion chamber. Flue dusts of solid substances are eliminated from burnt gas by classical technological processes, by cyclone clarifiers or by filters.

2.3. Steel plant dust
Steel plant dust is an industrial material produced in furnaces during the production of castings from grey iron or ductile cast iron. The gases from furnace contain solid particles that are trapped, condensed and trapped in electrostatic precipitators. It is a dry and loose material whose grains have a spherical shape and a maximum size of about 0.1 mm.

3. Experimental part
The objective was to verify the properties of fly ash(steel plant dust)-cement mixtures. Above all, their strength characteristics and frost resistance, depending on the amount of added fly ash (steel plant dust), which could be subsequently used for proposal of various kinds of composite materials for specific works. As a major component, to which 5%, 10% and 20% part of fly ash or steel plant dust was added, was chosen a fine cement, class C25.

The following types of secondary energy products were chosen: granular fly ash from power plant – granulating furnace, desulphurization by wet limestone method, fly ashes; fluid fly ash from power
plant – fluid furnace, fly ashes; steel plant dust – electrical precipitator. Constitution of individual composition:

Sample No. 1 – reference material, 100 % of fine cement;
Sample No. 2 – 5 % of granular fly ash + 95 % of fine cement;
Sample No. 3 – 10 % of granular fly ash + 90 % of fine cement;
Sample No. 4 – 20 % of granular fly ash + 80 % of fine cement;
Sample No. 5 – 5 % of fluid fly ash + 95 % of fine cement;
Sample No. 6 – 10 % of fluid fly ash + 90 % of fine cement;
Sample No. 7 – 20 % of fluid fly ash + 80 % of fine cement;
Sample No. 8 – 5 % of steel plant dust + 95 % of fine cement;
Sample No. 9 – 10 % of steel plant dust + 90 % of fine cement;
Sample No. 10 – 20 % of steel plant dust + 80 % of fine cement.

3.1. Produce of fresh and solid mortar mixtures and subsequent tests
Mixtures were produced in laboratory of building materials. Mixing of the mixture was carried out under laboratory conditions, temperature (20±2) °C and relative humidity (60±5) %. Sample of fresh mortar was prepared on prescribed value of spilling. The amount of water required to achieve the right consistency was determined on the basis of experimental tests. The water content of the mixture, suitable for grouting has always been determined so that the spill of the mixture performed by shaking table BetonSystem RS-15 in accordance with standard EN 1015-3 was 230 mm. The mixture was prepared by the MI-CM5A Concrete Mixer. The mixing time and speed were in accordance with EN 1015-2, it means mixing for 90 seconds at low speed.

Optimal mixtures were placed into moulds with dimensions 40x40x160 mm. The content was compacted in the middle of the mould by 15 strikes by rammer made from non-absorbent material square cross-section. The filled moulds for strength and resistance tests were aligned by spatula, covered by oiled glass and placed to humidity chamber with a prescribed humidity 95 % and temperature 20 °C. Two days later after mixing samples were took out from moulds and stored into environment with prescribed humidity. The strength characteristics were calculated from measured value of acting force at which the samples was broken. For testing was used press machine BetonSystem with a maximum load 10 kN for bending tensile strength and 300 kN for compressive strength with calibration till 05.03.2019. On samples were performed the following physico-mechanical properties: Determination of consistence of fresh mortar (by flow table) – EN 1015-3; Determination of air content of fresh mortar – EN 1015-7; Determination of bulk density of fresh mortar – EN 1015-6; Determination of flexural and compressive strength of hardened mortar – EN 1015-11; Testing of frost resistance of mortar – ČSN 72 2452.

4. Evaluation

4.1. Evaluation of fresh mortar mixture
The bulk density of each mixture is almost the same, but the amount of water required to achieve required consistency considerably vary. The highest amount of water is needed for optimal deflocculation of the mixture with the addition of steel plant dust and fluid fly ash. The air content decreases depending on the amount of added additive, which has a much smaller grain size for all three types of additives that results in better cement grain coating and reduced air volume in the mixture (table 1).
Table 1. Composition of each fly ash (steel plant dust)-cement mixtures and their essential characteristics.

| Sample No. | Cement fine [g] | C25 secondary energy product [g] | Water [g] | Water-cement ratio | Bulk density [kg m\(^{-3}\)] | Air content [%] |
|------------|-----------------|-----------------------------------|-----------|-------------------|------------------------------|----------------|
| 1          | 3000            | 0                                 | 570       | 19                | 2041                         | 5.4            |
| 2          | 2850            | 150                               | 540       | 18                | 2041                         | 4.9            |
| 3          | 2700            | 300                               | 540       | 18                | 2045                         | 3.9            |
| 4          | 2400            | 600                               | 540       | 18                | 2050                         | 2.4            |
| 5          | 2850            | 150                               | 600       | 20                | 2075                         | 4.4            |
| 6          | 2700            | 300                               | 660       | 22                | 2076                         | 3.0            |
| 7          | 2400            | 600                               | 780       | 26                | 2079                         | 2.0            |
| 8          | 2850            | 150                               | 600       | 20                | 2042                         | 4.2            |
| 9          | 2700            | 300                               | 705       | 23.5              | 2048                         | 3.8            |
| 10         | 2400            | 600                               | 900       | 30                | 2016                         | 1.8            |

4.2. Evaluation of solid mortar mixture

Verification tests of tensile strength in bending and compressive strength were performed on solid test specimens after 2, 7 and 28 days after mixing. Within the frost resistance test, the strengths tests were performed until the sample decay, maximum number was 100 test cycles. Before the final results were put into graphs, were corrected by calculating of statistical characteristic of random choice (arithmetic mean, standard deviation, variation coefficient), so that all of the strengths comply with interval X ± 3s.

Mixtures with additions of granular fly ash prove higher initial strength than the reference sample. This property may be caused by higher content of glassy phase that significantly affects the reactivity of fly ash with CaO. However, after 28 days these samples show lower strength than for reference sample. Mixtures with addition of fluid fly ash prove lower initial strength, but the strength after 28 days are higher than for reference sample that may be caused due to higher content of free CaO. For steel dusts is possible to notice with their increased value lower initial strength and also compressive and bending strength after 28 days. Is known improvement of strength characteristics for long term samples (3 months and more). Currently are in laboratory of building materials stored samples for verification of strength after 3 and 6 months.

![Figure 1. Increase of compressive strengths for all type of samples after 2, 7 and 28 days.](image)

For steel dusts is possible to notice with their increased value lower initial strength (figure 2) and also compressive and bending strength after 28 days (figure 1). Is known improvement of strength characteristics for long term samples (3 months and more). Currently are in laboratory of building materials stored samples for verification of strength after 3 and 6 months.
Figure 2. Difference between measured tensile strengths of samples subjected to frost resistance test and reference samples removed from climatic chamber.

Table 2. Coefficients of frost resistance to reference samples

| Number of freeze-thaw cycles | Type of sample  | 25  | 50  | 75  |
|------------------------------|-----------------|-----|-----|-----|
| Reference sample             |                 | 23 %| 9 % | 4 % |
| 5% gr.fly ash                |                 | 17 %| 9 % | /   |
| 10% gr.fly ash               |                 | 14 %| 5 % | /   |
| 20% gr.fly ash               |                 | 13 %| /   | /   |
| 5% fluid fly ash             |                 | 35 %| 20 %| 4 % |
| 10% fluid fly ash            |                 | 33 %| 17 %| 2 % |
| 20% fluid fly ash            |                 | 21 %| 4 % | /   |
| 5% steel plant dust          |                 | 16 %| /   | /   |

For frost resistance (table 2) was intended to expose samples to 100 freeze-thaw cycles divided into 4 periods. Final period was not achieved due to considerable decomposition of all samples. After 25 cycles, the resulting strength of all mixtures did not particularly distinct from the reference sample. Samples with 5% and 10% fluid fly ash prove about 25% higher values than strength of reference sample. For mixtures with 20% granular and 20% fluid fly ashes and 5% steel dust fine cracks have been occurred on surface in length up to 5 mm and deep maximally 1 mm. For samples with 20% of fluid fly ash occur the crumbling of edges of the sample.

After 50 freeze-thaw cycles the 5% and 10% fluid and 5% granular fly ash prove higher strength than reference sample. Strengths for mixtures with 20% of fluid fly ashes decreased in comparison with reference sample about more than 50%, strengths of mixtures with 20% granular fly ash and 5% steel plant dust was not possible to measure, for these samples instead of fine cracks occurred the distortion of whole sides.

Performed 75 cycles was reached only with 5% and 10% fluid fly ashes, with very low but comparable strengths in comparison with reference sample.

5. Evaluation of experimental part

The main aim of the thesis was to verify the influence of secondary energy products and their relative proportions in the mixture (granular and fluid fly ashes produced by power plants, steel plant dust) to the resulting rheological properties of the mixture. At the same time was observed their effect on the development of tensile strength and compressive strength in different times and after freeze-thaw cycles. On the basis of obtained results, is possible to state, that if are not required rapid increases of initial strengths is possible to make cement mixes with up to 20% compensation of fine cement by a suitable type of secondary energy product (mainly granular or fluid fly ashes, but also steel plant dust). The tensile strengths in bending and also compressive strengths are not significantly affected. Using of
this substitute is possible to assume cost reduction in comparison with reference mixture. **Fly ashes:** If is the main aim to achieve higher initial strengths of ash-cement mixtures to mixtures without fly ash, is necessary to reduce the value of water coefficient, which subsequently affects the workability. The fine fraction of used fly ash with higher specific surface area contributes significantly to get higher values of strengths. It is generally known that the negative influence of the aggressive environment on the life cycle of the grout is possible to restrain by the addition of fly ash. The positive effect is mainly observed in fly ash mixtures exposed to sulphate solutions. **Steel plant dust:** For test mixtures with steel plant dust, the initial strengths increased slowly. Although the strengths after 2, 7 and 28 days showed low values, according to available information’s, the resulting 90 days strengths, respectively 150 days strengths of the mixture were comparable with strengths of reference mixture after 28 days.

Due to presence of steel plant dusts in tested mixtures, retardation was observed during setting, especially in first 24 hours, during which the setting of fresh mortar was very slow. The effect of retardation begins to retreat after 48 hours of aging. The presence of dusts prove after approximately 7 days when the strength of mixtures with 10% and 20% part of dust already show lower differences to reference mixture.

**6. Conclusion**

Use of mixtures with high mentioned additions should always be considered, especially according to place of use, conditions which affect location and with properties we want to achieve. For general recommendation of possible use as a substitution of cement in mixtures is certainly advisable to perform several other tests, e.g. determination of permeability, determination of adhesion and heat expansion, determination of initial and final setting times under higher temperatures or resistance to aggressive environments. It would also be worthwhile to research the ecological burden of secondary energy products on environment, especially after the end of its life cycle. Known is facile leachability of toxic metals such as arsenic or chromium or extremely high pH values for water waste.

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