Utilization of fuel oil ash in injection solutions

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Abstract. Injection solutions are used to fix the soil in the underground constructions, which requires significant cement expenditure. The study has found that cement can be substituted with up to 40% of ash from the high-sulphur fuel oil combustion by putting it into injection solutions. During the solution preparation, the ash releases up to 90% of sulphur. The sulphur in the alkaline solution undergoes disproportionation with the production of nanoparticles that fill the cavities in the crystallizing cement stone. This gives cement strength while its amount in the mixture is reduced. The modifier-ash solution ensures ecological safety, which has been proved by measuring phytotoxicity on the radish seeds Raphanus sativus germination.

1. Introduction

Ash is formed as a part of production waste, when using boilers running on fuel oil. Such ash is considered as one of the hazardous substances for the environment [1]. Fuel oil ash forms dust, which is added to the distribution of suspended particles containing harmful pollutants like heavy metals over long distances. This causes air dusting, and as a result, ash particles enter the respiratory system of people, provoking allergic reactions and diseases of the upper respiratory tract. In addition, the spread of ash particles over long distances leads to dangerous technogenically transformed landscapes and a negative impact on the environment [2-4].

These days, composite injection solutions are used to strengthen soils, cracks, and fractures in transport construction. These solutions are made out of various types of waste, such as fly-ash emitted during solid fuel combustion and the burning of spent wooden sleepers (i.e. railroad ties) [3].

The main component in the composite solution formula is cement, the cost of which is constantly growing. One of the studies aimed at reducing consumption of cement and improving its physical and chemical properties is the injection of various mineral additives that activate hardening processes of cement. The most promising research studies the use of ash as a component of cement, due to a homogeneous distribution of ash particles in cement volume [4]. In addition, it is suggested to replace some part of the Portland cement with ash in the production of concretes and mortars [5, 6]. Fly ash has been widely used for the preparation of cement. It represents the smallest ash particles formed after combustion of solid fuel materials at a heat power plant. Fly ash can be used to improve the quality of concrete, as well as to prevent its waste. Currently, replacement of 25-30% of Portland cement with fly ash has been proved effective for the quality of concrete. With such a replacement, the strength of concrete is practically the same as that of concrete without ash. This was proved during the construction of the Bratsk hydroelectric dam and the Dnieper hydroelectric complex. In Germany, about 4 million tons of fly ash per year is used for producing mortars, ferroconcrete goods, and other materials containing cement [1].
The use of ash additives generates composite solutions with improved technological performance. In the production of injection solutions used in transport construction, bentonite-cement solutions are usually used [5, 6]. Due to the uniformity of its chemical composition, the ash generated during combustion can be used to partially replace cement in composite systems. In addition, ash disposal aims at environmental protection by eliminating harmful emissions into the environment. However, a widespread use of ash is possible only after complete neutralization of the toxic elements it contains in order to prevent them from leaching and entering adjacent environments.

Therefore, it is probably possible to use the ash from burning fuel oil for composite solutions in transport and underground construction. Previously, it was found that it is possible to replace 40% of cement with ash without losing the technological parameters of the resulting composite solution. According to this technology, the solution was prepared by mixing all the components [4, 7-9]. However, in practice, this method proved to be ineffective. In the production of composite solutions, it is easier to use a pre-mixed dry blend containing bentonite, ash, and cement.

The article aims at confirming experimentally the possibility of using ash from burning fuel oil as a structuring additive to composite solutions. This technology will help to save cement in the production of building materials without compromising their strength and solve environmental problems as well.

2. Methods
The article deals with the possibility of using ash from burning fuel oil as a structuring additive for partial replacement of cement in composite injection solutions [10].

The ash from furnace fuel oil (FFO) combustion was used in this study. The chemical composition of the fuel oil ash after burning includes oxides and hydroxides, %: MgO – 0.22; K₂O – 0.06; P₂O₅ – 0.06; Fe₂O₃ – 51.23; MnO – 0.501; V₂O₅ – 1.54; TiO₂ – 0.03; CaO – 0.71; SiO₂ – 1.49; Al₂O₃ – 0.48; Na₂O – 0.14 and heavy metals, ppm: Ba – 105; Cu – 590; Zn – 148; Pb – 131; Cr – 216; As – 11; Sr – 23; Ni – 6997; Cl – 1123; Nb – 10; S – 143100; Y – 3; Th – <5; U – <5; Zr – 30; Rb – 9; Co – 100.

Taking into account the chemical composition of the ash, its hazard class for the environment and human health is calculated. It proved to belong to Hazard Class 3 (substances dangerous for human health) and Hazard Class 4 (dangerous for the environment) [11].

Soda-modified bentonite clay of the P2T2A brand, with a montmorillonite content of 75-80 % and a sorption capacity of 113.3 mg * EQ/100g was used for the research, as well as cement of the M500 brand and liquid glass (density – 1.46 g/cm³, silicate module – 2.7-3.4%).

The study shows the effect of ash additives on changes in the rheological properties of cement-bentonite solutions during the curing process at a 2:1 water-cement ratio in the presence of 5 % liquid glass, where the cement was replaced with ash, the amount of which varied from 2 to 50 % [12, 13].

Such changes in the structure formation of solutions were performed in order to study the possibility of replacing cement with ash in a composite solution. The amount of ash varied from 1 to 50 %. The strength of composite solutions was determined with a hydraulic press “Controls 50-C0050/CAL50” (Italy).

In order to make a composite solution, liquid glass was blended into the mixture of bentonite and cement with ash while stirring.

3. Results and discussion
An increase in strength of the solution with up to 40 % of ash is observed within 28 days, while further additions of ash to the solution lead to its decrease (Fig. 1).

The change in the structuring rate of the composite solution, where 40 % of cement is replaced with ash, and the increase in strength are due to sulphur leaching from the ash during the preparation of the composite solution. In an alkaline solution, sulphur undergoes disproportionation with polysulphides and thiosulphates production, followed by formation of sulphur nanoparticles with average size of 20-25 nm [8, 9]. This apparently causes a change in the structuring kinetics.
Figure 1. Strength of composite solutions within 28 days after preparation versus ash concentration in the mixture.

In order to confirm this assumption, a model experiment was performed. The ash was placed in the medium (pH = 12) appeared when the components were mixed. Then, the content of sulphates in the filtrate was determined at certain intervals, using a UNICO 2800 spectrophotometer. During the preparation of the composite solution, which takes approximately 20 minutes, almost 90% of the sulphur passes into the composite solution. Figure 2 shows that approximately 93% of the equilibrium amount is achieved after 20 minutes of leaching when mixing ash with an alkaline medium. The change in the structuring of composite solutions with various ash additives is caused by the ability of sulphur to disproportionate in alkaline solutions and the subsequent formation of nanoparticles [3]. These nanoparticles eventually grow to highly dispersed colloidal sizes and fill in the cavities of the crystallizing cement stone, forming a monolith.

Figure 2. Kinetics of sulphur leaching from ash.

In order to confirm the structuring of a composite solution containing ash at a various water-cement proportions (from W/C 2:1 to 1.33:1), strength was determined with an ultrasonic concrete strength meter “PULSAR 1.1”.

It turned out that the speed of ultrasonic waves passing through the composite solution containing ash was 1.4 higher than the control sample, which indicates the material structure compression and the creation of additional contacts between the particles [14].

The environmental safety of the composite solution where 40% of cement is replaced with ash was determined on water extracts from composite solutions. It was also tested on the seeds sprouts of the
radish *Raphanus sativus*. The results of the toxicity study show that the composite sample with the ash additives has the level of phytotoxicity almost equal to that of the control sample.

4. Conclusion
The use of fuel oil ash in the production of composite solutions is justified by environmental and economic aspects. It helps to reduce the cement consumption, an expensive component in mortars and concretes, without compromising the characteristics of the resulting material. At the same time, this technology helps to reduce the costs of setting up and operating ash dumps, and to solve environmental problems associated with ash contamination of the atmosphere, water, and soil.

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