

ECOLOGICAL COMPOSITE MATERIAL WITH OIL SHALE ASH PARTICLES. MECHANICAL PROPERTIES

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Abstract. The need for “ecological” and “green” materials is increasing because of the strong demand to reduce the speed of climate change and decrease carbon footprint of human activities in nature. In the cement production process high amount of CO₂ is obtained as by-product. In the present research cement in a concrete mix is partially replaced by oil shale ash (OSA). OSA is a by-product itself, so utilisation of it also positively affects the environment. OSA particles have different size, and fabricating of such “ecological” concrete composite material with the concrete matrix reinforced by OSA particles is obtained. Similar situation is obtained during reinforcement of epoxy resin by OSA particles. Obtaining particle reinforced composite, the problem of precise prediction of the composite material averaged elastic properties appeared. The particles have different size, shape and are chaotically distributed in the concrete volume. Elastic properties averaging methods – theoretical models, including the rule of mixtures Voigt method, rule of mixtures Reuss method and Halpin–Tsai method, were used. Results were compared with experimental data. For that, samples (prisms 40x10x10cm) of concretes having cement replaced by 0%, 10%, 15%, 20%, 25%, 30%, 35% of OSA were fabricated and tested by the four-point bending test. The results that were obtained showed that the rule of mixtures Voigt and the rule of mixtures Reuss method as well as Halpin-Tsai methods generally slightly underestimate the value of elastic modulus for concrete-OA, whereas the Mori-Tanaka and Halpin-Tsai methods provided closer predictions.

Keywords: oil shale ash, concrete, composite, elastic modulus.

Introduction

The rising global demand for energy has become a reason of the wide usage of fossil fuels. Each fossil fuel type has different influence on environment but all of them are leaving carbon footprint. One of these fossil fuels is oil shale ash (OSA). However, oil shale is a low calorific fuel and produces a significant amount of OSA during burning. There is some amount used as constituent to Portland cement, road construction or for agricultural purposes but 98% of it is still landfilled [1; 2]. OSA composition varies depending on the combustion process and oil shale properties. Two most widespread methods of burning of oil shale are pulverized firing and circulating fluidized bed [3]. The pulverized firing technology uses pulverized oil shale powder in furnace burning it. Temperature from burning heats the water (steam) that rotates the generator turbines. During the burning process, OSA is forming. In case of the circulating fluidized bed high temperatures are not needed. Machined oil shale particles are fed into the chamber with fluidizing gas blowing from the bottom (fluidized bed) and moving particles to the top of the chamber. Temperature can be slightly more than the oil shale ignition temperature. Comparing to the pulverized firing method temperature (around 1350-1400 °C), it is much lower for the circulating fluidized bed method (around 750-950 °C). The advantage of this method is that the burning particles are circulating in the chamber making the burning process cleaner and more efficient [3; 4]. Starting from 2018 OSA is not classified as toxic material [5-8].

This makes broad usage of OSA possible. OSA as a binder has air, pozzolanic or latent hydraulic properties. One of the main applications of OSA is in the building industry. Alaloul et al. (2021) [9] made a systematic review showing the potential of OSA as a supplementary cementitious material in concrete and mortar production. Due to its pozzolanic properties, OSA can replace cement partially or fully as an environmentally friendly solution. However, challenges such as variability in composition and many dependent factors on quality and properties of OSA makes it difficult.

In the study by Kou, S. and Poon, C. [10] a compressive test of concrete specimens was conducted. The specimens were 100 mm cubes and 100 mm diameter, 200 mm height cylinders. The cubes were for the compressive strength test and the cylinders were used to test the tensile splitting strength. Fly ash properties in the study by Kou, S. and Poon, C. are close to the properties of OSA. Cement from the concrete recipe was partially replaced by fly ash. The replacement by fly ash was in amounts of 0%, 25%, 35%, and 55% by weight. The compressive strength decreased with the increase in fly ash in the concrete mixtures. In the study done by Farooq, U. [11], concrete specimens in which cement was partially replaced by fly ash were made and compressive tested. Fly ash replaced cement in proportion

of 0%, 30%, 40%, and 50% by weight. The specimen was tested after 28 days of curing. Compressive strength of the specimens decreased as the amount of fly ash replaced increased. Soni, D. K. et al. [12] also studied fly ash properties as partial replacement of cement in concrete. Samples with 0%, 30%, 40%, and 50% fly ash replacement of cement in concrete were tested. The samples were aged for 28 days. Compressive strength of the specimens decreased as the amount of fly ash replaced increased similarly as in previous studies.

According to Noguchi, T. and Tomosawa, F. [13], the elastic modulus value is sublinear dependent on the compressive strength of the specimens tested thus decreasing the compressive strength means decreasing the elastic modulus.

Materials

OSA is a powder- like substance (Fig. 1.) with mixed contents. Contents of each batch depend on the properties of the oil shale and storage conditions. It has a porous structure and spherical shape. The mode value (most repeated value) of the diameter of one particle is 30-110 micrometres [14].



Fig. 1. Oil shale ash

OSA for this study was collected from the Auvere power plant. Mechanical properties were studied in [15-17], they are given in Table 1.

Table 1

Properties of OSA

Property	OSA
Density	2630 kg·cm ⁻³
Elastic modulus	16 GPa
Poisson's ratio	0.3

Chemical composition of the OSA from the Auvere power plant was studied by Kalpokaitė-Dičkuvienė, R. et al. [18] and is given in Table 2.

Table 2

Chemical composition of OSA

Compound	Percentage of weight, %
CaO	38.77
SiO ₂	22.07
Al ₂ O ₃	7.9
K ₂ O	3.81
Fe ₂ O ₃	3.83
MgO	2.47
SO ₃	3.83
TiO ₂	0.53
Na ₂ O	0.16
P ₂ O ₅	0
MnO	0

Cement *Schwenk CEM I 42,5 N* was used. Concrete prisms were prepared using the recipe in Table 3.

Table 3

Specimen recipes

Material, kg	CM0	CM22-2II	CM23-II	CM24-II	CM25-II	CM26-II	CM27-II
Cement 42.5	5.5	4.95	4.675	4.4	4.125	3.85	3.575
OSA	(0%) 0	(10%) 0.55	(15%) 0.825	(20%) 1.1	(25%) 1.375	(30%) 1.65	(35%) 1.925
Water	5	5	5	5	5	5	5
Gravel 4-8 mm	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Sand 0.3-2.5 mm	21	21	21	21	21	21	21
Sand 0-1.0 mm	12.6	12.6	12.6	12.6	12.6	12.6	12.6
Dolomite	4.8	4.8	4.8	4.8	4.8	4.8	4.8
Plastificators	0.14	0.14	0.14	0.14	0.14	0.14	0.14
Microsilica	0.3	0.3	0.3	0.3	0.3	0.3	0.3

All the solid components were mixed in a rotating concrete mixer. Plastificator and water were mixed separately and then added in two steps into the concrete mixer. Also fiber concretes with OSA were investigated in [19-22].

Experimental setup

A four-point bending (4PBT) testing machine was used to find the bending properties of the concrete. Tests were carried out according to the LVS EN 12390-5:2019 standard. A 40 cm prism with 10 cm thickness and 10 cm width was loaded in two points and supported in two points. Four specimens for seven recipes were produced and cured for 28 days. In total twenty-eight specimens were tested and none of them was excluded from analysis.

The experiment was performed on the Controls Model 50 – C0050/CAL5 test machine. The schematic view (all numerical values are in mm) of loading is shown in Figure 2. Displacement sensors were installed from both sides in the middle of the prism between the pushing rollers. One support roller (bottom) and one pushing roller (top) that are closest to the observer in Figure 3 have an extra axial degree of freedom.

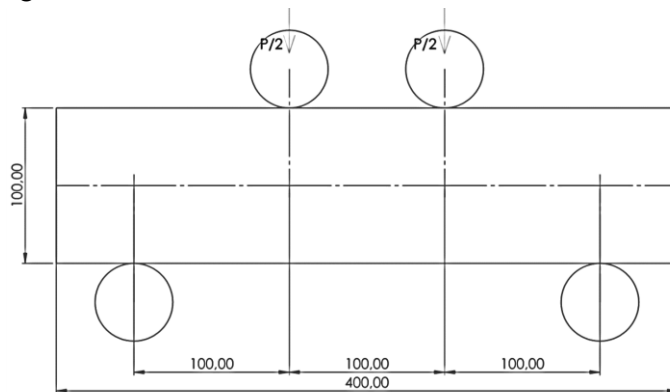


Fig. 2. 4PBT setup configuration



Fig. 3. 4PBT setup photo

The results were recorded by pressure sensors at the pushing roller part and displacement sensors at the specimen sides between the pusher rollers. The obtained results were analysed using MS Excel software. Linear approximation equations from linear sections of the stress-displacement data plot were obtained during the experiment for finding the average applied force value. Further that value will be used for obtaining the elastic modulus of the concrete prism and comparison of the results.

Determination of elastic modulus

After obtaining the average applied force, using the unit force approach for displacement (integral) calculation of elastic beams under bending and setup configuration schematics in Fig. 2, it is possible to find the equation for the elastic modulus calculation:

$$E = \frac{23 \times P}{4 \times a \times \Delta'} \quad (1)$$

where E – elastic modulus, Pa;
 a – one third of the distance between rollers (100 mm on Fig.2.), m;
 Δ – displacement of bending, m;
 P – applied force, N.

The obtained elastic modulus is indirectly found value of the elastic modulus.

Theoretical elastic modulus determination by the rule of mixtures (Voigt modulus)

There are two main methods of composite material model representation. In the representative unit volume, the matrix-reinforcement-matrix is loaded longitudinally and transversally. Longitudinally means that the matrix and reinforcement have the same elongation and same force applied. Transversally means that the matrix and reinforcement have different elongation and different force applied. The longitudinally applied force case is called Voigt modulus and the transversally applied force case is called Reuss modulus. More detailed it is described in the book of Kaw, A.K [23] subsection 3.3.1. Applying the Voigt modulus, equation 2 is composed [24]:

$$E_{VM} = E_{concrete} \times V_{concrete} + E_{osa} \times V_{osa}, \quad (2)$$

where $E_{concrete}$ – elastic modulus of plain concrete, Pa;
 $V_{concrete}$ – volume fraction of plain concrete, unitless;
 E_{osa} – elastic modulus of OSA, Pa;
 V_{osa} – volume fraction of OSA, unitless;
 E_{VM} – elastic modulus by Voigt, Pa.

Theoretical elastic modulus determination by rule of mixtures (Reuss modulus)

Applying the Reuss [25] modulus, equation 3 is composed:

$$E_{RM} = \left(\frac{V_{concrete}}{E_{concrete}} + \frac{V_{osa}}{E_{osa}} \right)^{-1}, \quad (3)$$

where $E_{concrete}$ – elastic modulus of plain concrete, Pa;
 $V_{concrete}$ – volume fraction of plain concrete, unitless;
 E_{osa} – elastic modulus of OSA, Pa;
 V_{osa} – volume fraction of OSA, unitless;
 E_{RM} – elastic modulus by Reuss, Pa.

Theoretical elastic modulus determination by the Halpin-Tsai method

The Halpin–Tsai equation [26] gives a semi-empiric way to estimate the mechanical properties of composite materials depending on several properties of the filler particles such as the shape and volume fractions. The elastic modulus, according to the Halpin–Tsai equation, is given by

$$E_{HP} = E_{concrete} \cdot \frac{1 + \zeta \cdot \eta \cdot V_{osa}}{1 - \eta \cdot V_{osa}}, \quad (4)$$

where ζ – shape factor for the spherical filler's particle shape, unitless;
 η – coefficient depending on the elastic parameters of the matrix, filler, and shape of the filler, unitless;
 E_{osa} – elastic modulus of OSA, Pa;
 V_{osa} – volume fraction of OSA, unitless;
 E_{RM} – elastic modulus by Reuss, Pa.

The parameters ζ and η can be found using equations (4) and (5), which are given below.

$$\zeta = 2 + 40 \cdot V_{osa}^{10}, \quad (5)$$

$$\eta = \frac{E_{osa} - E_{concrete}}{E_{osa} + \zeta \cdot E_{concrete}}, \quad (6)$$

The obtained results by utilizing these methods will be discussed in the section below.

Results and discussion

Experimental results of the four-point test are shown in Figure 4. As seen in Figure 4 below, it is impossible to track a dependence between the amount of OSA and the bending strength of the concrete prisms.

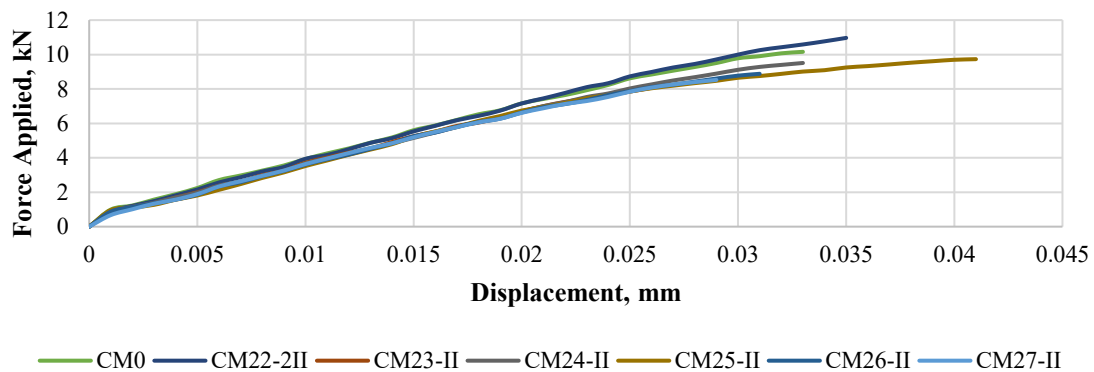


Fig. 4. Experimental results of four-point tests

Elastic modulus from the experimental results was obtained by using equation 1 and linearization of the linear part of the experimental data. The results obtained by the experiment are not varying a lot. The main reason for it is a very small volume fraction of OSA in the concrete. As it can be seen in Recipes Table (Table 3) cement and OSA itself take around only 11% of the weight. Other components content and amount are constant for every set of the OSA concentration. The comparison of the theoretical and experimental elastic modulus outputs is shown in Figure 5. Comparison of only theoretical values is shown in Figure 6.

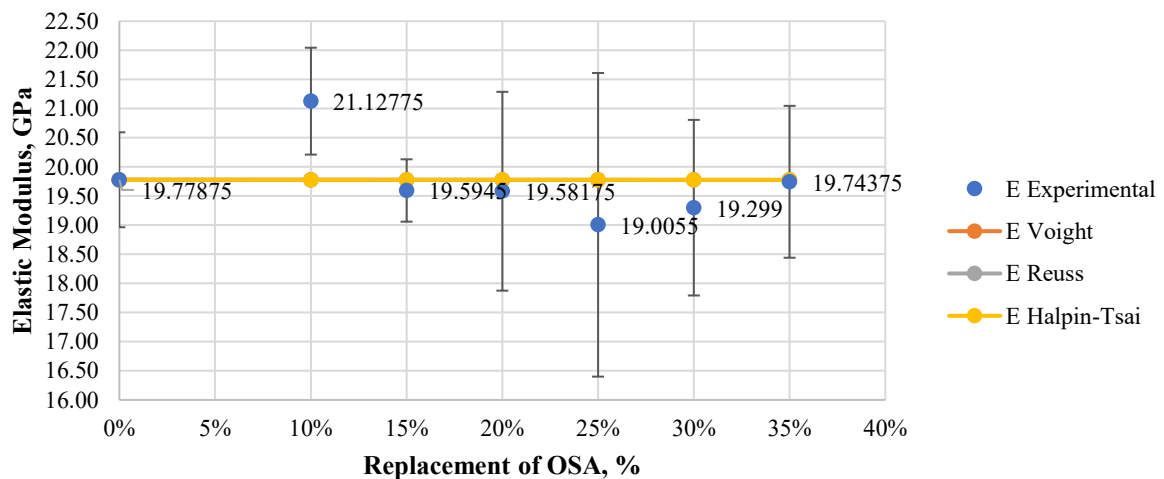


Fig. 5. Results

In case of the Voigt method, it is possible to see that linearly increasing amount of OSA linearly decreases the elastic modulus of the concrete. In the Reuss method it decreases even more with addition of OSA instead of cement. In case of the Halpin-Tsai method it is possible to observe the same decreasing elastic modulus with increasing the OSA concentration. All theoretical methods have the same correlation. Mathematical approximations of the mentioned methods can be found in [27; 28]. Experimentally the elastic modulus first increases till 10% of concentration, then parabolically decreases, peaks at 25% of concentration and then increases again till 35% of concentration. One of the

reasons of such behaviour is the non-consistent contents of OSA. But in general, the elastic and strength properties are decreasing. This happens because the elastic modulus of the cement is higher than the elastic modulus of OSA. So, studies by Kou, S. and Poon, C. [10], by Farooq, U. [11] and Soni, D. K. et al. [12] also obtained decreasing of elastic and strength properties of concrete with increasing of the OSA.

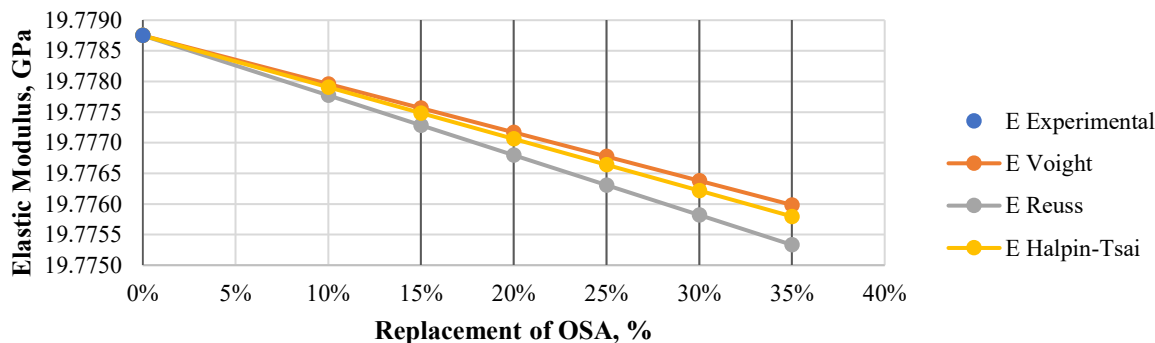


Fig. 6. Results of theoretical calculations

Conclusions

1. Small amounts of OSA are slightly improving the mechanical properties of the concrete mix, adding more OSA decreases the strength and elastic properties of concrete.
2. Decrease in the strength in the elastic modulus is reaching 0.18% comparing with the initial material (OSA amount 0%), when OSA amount is reaching 35%. It allows to use small amounts of OSA as cement replacement without major change in the mechanical properties.
3. Utilization of OSA in concrete gives the second life for it.
4. The performed experimental investigation by bending of concrete with cement partially replaced by OSA has shown similar results to investigations made by compression testing published earlier as mentioned in the materials section.

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Author contributions

Contribution of each author: conceptualization, A.G. and I. J., methodology, I.T. and L.Š., software, I.J., validation, I.J., formal analysis, A.G. and I.T., investigation, I.J., L.Š. and I.T., data curation, I.J., writing – original draft preparation, I.J., writing – review and editing, I.J. and A.G., visualization, A.G. and L.Š., project administration, I.J., funding acquisition, I.J. All authors have read and agreed to the published version of the manuscript.

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