Cement-based materials with oil shale fly ash additives

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Abstract. Experimental studies on the influence of oil shale fly ash additives on thermal expansion, strength, shrinkage, and heat release of concrete were carried out. The addition of 30% fly ash over cement content increases the thermal expansion by 6 times. The addition of 40% fly ash increases the thermal expansion by 16 times. The expansion is due to the high free calcium oxide content (10%) in the fly ash and the high sulfuric acid anhydrite SO₃ content (10.3%). The anhydrite forms a highly expanding calcium hydrosulfoaluminate upon reaction with tricalcium aluminate cement in an unlimited amount of water. The oil shale fly ash addition above cement content significantly reduces shrinkage. If the ash content is higher, then the shrinkage decreases more. Shrinkage is on average 1.3 times less at a 30% fly ash content, and shrinkage is 1.8 times less at a 40% fly ash content. The fly ash has a higher sorption capacity than cement. Samples with the oil shale fly ash addition absorb more moisture than mixes without fly ash. Oil shale fly ash increases the compressive strength. If the fly ash content is 30% by weight of cement, then the compressive strength is higher than if the fly ash content is 40% by weight of cement for all concrete hardening periods. The flexural strength of mixes containing the fly ash turned out to be lower than the flexural strength of the mix without fly ash in the initial period of up to 15-22 days. Mixes with fly ash content in the amount of 30% and 40% by weight of cement exceeded the flexural strength of the mix without fly ash, respectively, by 24 and 17%. The fly ash addition provides a calmer, extended in time heat release with low self-heating of concrete in the initial period from 1 to 3 days. That is especially valuable for the thermal crack resistance of concrete.

1. Introduction
Ash dumps are a source of an increased environmental hazard. They hurt human health, ground and surface water, atmosphere, flora, and fauna. Oil-shale deposits are found in many parts of the world. Total resources of oil-shale deposits are estimated at 411 billion tons of in-place shale oil. [1].Oil shale fly ash is used for concrete production [2], [3]. The use of fly ash in concrete dates back to the late 20th century and its advantages and disadvantages had been widely researched.

Despite the broad-based research carried out across the globe in utilizing fly ash as a cement replacement material in concrete, the level of replacement is still limited to a maximum of 35% of cement by mass [4].

Oil shale fly ash additive on asphalt mixes was studied. Replacing 10% of the mineral filler by fly ash proved to be the most effective percentage in improving the mechanical properties of asphalt mixes [5].

Oil shale fly ash can be converted into glass-ceramics [6]. The maximum mechanical properties of glass-ceramics’ compression strength are 186±3MPa, bending strength is 78±6MPa. Oil shale fly ash glass-ceramics has good chemical resistance, and low heavy metals leaching concentrations. It could be used as a substitute material for construction applications.

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The use of fly ash in the concrete production can be divided into two types. The first type is as a coarse aggregate [7], [8], [9] and the second one is mineral filler for partial or complete replacement of cement [10], [11], [12], [13].

High-calcium oil shale fly ashes (HCOSFA) from Spain, Greece, Turkey, France, Estonia, Israel, Jordan, and other countries contain up to 43–60% CaO [14], [15]. In the paper [16], the use of fly ash in structural concrete was considered. It was demonstrated how a host of engineering properties of concrete, especially its durability were improved with the incorporation of fly ash. Besides, the author discusses the modes of fly ash use - as factory-produced blended cement and as a partial replacement of ordinary Portland cement in ready-mixed concrete plants.

Hydration and strength development of binder based on high-calcium oil shale fly ash and low-calcium coal fly ash was studied [14]. The compressive strength of fly ash binder is determined by the ratio of high-calcium oil shale fly ash and low-calcium coal fly ash, as well as by the water-cement ratio. The influence of curing conditions on long-term stability was also studied by this author [17].

Building blocks can be made from oil shale fly ash cementless binder. An initial increase up to three months and later reduction in strength of blocks were noticed. The disintegration of the hardened blocks was related to the transformation of ettringite which is one of the most important crystal phases of a cured binder [18]. It was found that ettringite is not stable under ambient air influence and over time the amount of ettringite was diminished. This resulted in a continuous strength loss of specimens containing only high calcium oil shale fly ash [19]. In [20] the variability of fractional, chemical and mineralogical compositions of oil shale fly ash was studied. A strong influence of CaO_free content on concrete strength was confirmed.

However, no data on oil shale fly ash binders’ thermal expansion and heat release was found in the available publications. This makes further research necessary. This research aims to study of linear expansion and shrinkage, strength, and heat release of concrete based on Portland cement and oil shale fly ash.

2. Materials and Methods

2.1. Testing laboratory
Fly ash aggregates were tested in Polytech-SKiM-Test laboratory of Peter the Great St. Petersburg Polytechnic University (Russia).

2.2. Concrete materials
For the production of concrete, the following materials were used:
1. Portland cement CEM I 42.5N manufactured by Oskolcement JSC (Belgorod region, Russia).
2. Natural sand. The sand has fineness modulus from 2 to 2.5.
3. Oil Shale Fly Ash Additives “Zolest-bet”. Bulk density is 1100±50 kg/m³; true density is 2850±50 kg/m³; specific area is 300-350 m²/kg. The chemical composition of the shale ash is presented in Table 1.

Table 1. The chemical composition of the shale ash “Zolest-bet” [%].

|        | SiO₂ | CaO | CaO_free | MgO | Fe₂O₃ | Al₂O₃ | SO₃ | K₂O | Na₂O | Ignition loss | Chlorides |
|--------|------|-----|----------|-----|-------|-------|-----|-----|------|--------------|-----------|
| 27.8   | 36.6 | 10  | 4.29     | 4.19| 7.02  | 10.3  | 4.26| 0.087| 4.87 | <0.1         |           |

Oil Shale Fly Ash Additives “Zolest-bet” is produced by Enefit Energiatootmine AS (Estonia) on two oil shale-fired thermal power plants, Eesti Power Plant (Eesti Elektrijaam) and Balti Power Plant (Balti Elektrijaam). This fly ash is a mineral residue from the combustion of oil shale at temperatures of about 1300–1400 °C. Ash consists of clinker phases, mainly dicalcium silicate, monocalcium aluminate, fine-grained free calcium oxide, calcium sulfate. The average grain size is 12-25 microns.

2.3. Concrete mixtures
Concrete mixtures were produced using a standard concrete mixer for 90 seconds.
Concrete mixtures are presented in Table 2.
Table 2. Concrete mixtures.

| Materials       | Mix No. 1 | Mix No. 2 | Control Mix No. 3 | Mix No. 4 | Mix No. 5 | Control Mix No. 6 | Mix No. 7 | Control Mix No. 8 |
|-----------------|-----------|-----------|-------------------|-----------|-----------|-------------------|-----------|-------------------|
| Cement          | 850       | 850       | 850               | 470       | 470       | 470               | 400       | 500               |
| Sand            | 913       | 827       | 1180              | 1387      | 1348      | 1498              | 1500      | 1500              |
| Shale ash “Zolest-bet” | 250       | 340       |                   | 140       | 190       |                   | 100       |                   |
| Water           | 279*      | 284*      | 260*              | 259       | 259       | 259               | 250       | 250               |
| Total           | 2292      | 2301      | 2290              | 2256      | 2266      | 2226              | 2250      | 2250              |

* amount of mixing water was selected so that the cone flow diameter was from 140 mm to 150 mm by Russian State Standard GOST 310.4.

2.4. Thermal expansion and shrinkage measurements
Concrete mixes No 1, 2, 3 were used in these tests. From each mix, 6 beam samples with a size of 40x40x160 mm were made. 3 samples were for thermal expansion measurement and 3 other ones were for shrinkage measurement. Samples were made in special molds, making it possible to lay metal inserts at the ends of the samples for measuring shrinkage and thermal expansion. After that, the samples in the molds were stored in a normal hardening chamber at a temperature of (20 ± 2) °C and relative humidity (95 ± 5) %.

Samples were removed from the mold one day after their manufacture. After that, the length of the samples was immediately measured using a device with a dial gauge. The value of the division was 1 μm (see Figure 1).

In the thermal expansion test, the samples always were in a water bath with a controlled temperature (20 ± 0.5) °C. The samples were removed from water only for the duration of the measurement.

In the shrinkage test, the samples were in a climatic chamber at a temperature of (20 ± 2) °C and relative air humidity (60 ± 5) %.

2.5. Compressive strength and flexural strength measurements
Concrete mixes No 4, 5, 6 were used in these tests. From each mix, beam samples with a size of 40x40x160 mm were made. 3 samples were for compressive strength test and 3 other ones were for shrinkage measurement. Samples were removed from the mold one day after their manufacture. After that, the samples were placed in a water bath with a constant temperature (20 ± 0.5) °C. Samples were removed from the bath only for the duration of the measurement.

2.6. Rate of heat release measurement
The effect of “Zolest-bet” shale ash on the heat release rate of concrete based on Portland cement CEM I 42.5 N was investigated.

Heat release Q was determined according to EN 196-9:2010. The heat release of concrete was determined by the thermos method at an initial temperature of 20 °C. After that, the heat release of concrete was recalculated to the isothermal hardening mode at a temperature of 20 °C.

We used the hypothesis in which ratio of the heat release rates and corresponding terms remains constant at moments of equal heat release at $Q_1 = Q_2$:

$$\frac{(\partial Q/\partial \tau)_2}{(\partial Q/\partial \tau)_1} = \frac{\tau_2}{\tau_1} = f_1 = \text{const}$$  (1)
The temperature function $f_t$ was calculated by the formula:

$$f_t = 2 \frac{t_1 - t_2}{\varepsilon},$$

where $\varepsilon$ is the characteristic temperature difference. If $t_1 - t_2 = \varepsilon$, then $f_t = 2$. This means if the temperature rises by $\varepsilon$ degrees, the rate of heat release will double.

Three identical samples of each concrete mix were tested. The readings of the temperature sensors were recorded by the datalogger every 30 minutes.

3. Results and Discussion

3.1. Linear expansion test results

The test results of the concrete mixes No 1, 2, and 3 for the thermal expansion are presented in Figure 2.

Figure 2 shows that the control mix No. 3 free of high-calcium fly ash additive has a high degree of thermal expansion. This value is more than 1 mm / m for 120 days. This value is approximately 2 times greater than usually in real concrete. Such the expansion, in all likelihood, is caused by a high cement content (840 kg / m$^3$), which also exceeds the usual values by an average of 2 times.

The addition of 30% fly ash over cement content (mix No. 1) increases the thermal expansion by 6 times, and the addition of 40% fly ash (mix No. 2) - by 16 times. The chemical composition has an increased content of two oxides (see Table 1), the expanding effect of which is well known. One of them is free calcium oxide CaO (10%), which forms calcium hydroxide with a volume of 2-3 times greater during hydration. Another one is sulfuric acid anhydrite SO$_3$ (10.3%). It forms a highly expanding calcium hydrosulfoaluminate upon reaction with tricalcium aluminate cement in an unlimited amount of water.

Curves mix No. 1 and mix No. 2 (see Figure 2) have three characteristic sites:

1) the initial site (up to 40 days). There is a rapid increase in expansion;
2) the site of a practical lack of expansion growth due to completion of chemical processes (from 40 to 90 days);
3) the site of development of shrinkage (from 90 to 120 days).

If the processes in the first two sections are quite understandable, then the causes of shrinkage are difficult to explain. The only thing that can be said is that shrinkage phenomena are associated with the presence of shale ash since without it a third section is absent. If the processes in the first two sites are quite understandable, then the causes of shrinkage are difficult to explain. The only thing that can be said is that shrinkage is associated with the presence of oil shale fly ash, since without it, a third section is absent. Since if there is no fly ash, then the third section is missing (see Figure 2).
3.2. Shrinkage test results

The shrinkage test results are presented in Figure 3.

![Figure 3. Shrinkage of samples during air hardening with relative air humidity (65 ± 5)% and temperature (20 ± 2) °C.]

Figure 3 shows that the oil shale fly ash addition over cement content significantly reduces shrinkage. If the ash content is higher, then the shrinkage decreases more. Shrinkage is on average 1.3 times less at a 30% fly ash content, and shrinkage is 1.8 times less at a 40% fly ash content. The shrinkage decrease occurs due to the expanding effect of fly ash. The predominant effect of shrinkage ends by the 30-day period. After that, the expansion can exceed the shrinkage. There is an alternate change in the sign of the deformation. This may be due to fluctuations in air humidity and a change in the sorption humidity of the samples. Thus, increasing the concrete moisture and the connection of additional moisture to the calcium hydrosulfoaluminate leads to an increase in its volume. When additional moisture is bound by hydrosulfoaluminate, the predominance of shrinkage over expansion begins.

Since the change in deformation sign is most susceptible to samples containing fly ash, it can be assumed that the fly ash has a higher sorption capacity than cement. To verify this position, additional experiments were carried out.

Cement samples and “Zolest-bet” fly ash samples were dried in an oven to constant weight. Two portions weighing 160 g were taken from each sample after cooling in a desiccator over calcined CaCl₂. Then, each portion was placed in a desiccator over water for long-term storage at a constant temperature (20 ± 2) °C. At the same time, samples of half beam with a size of 40x40x160 mm remaining after the compressive strength test were prepared and tested in the same way. Easily separable fragments were removed from them before the test. Periodically, the samples were removed from the desiccator and weighed to fix the weight increment.

The test results are shown in Figure 4.

![Figure 4. Sorption moisture test results of the samples.](image)
The curves in Figure 4 show that fly ash has the highest sorption capacity. The experimental mixes No.3, No.3, and No.1 slightly exceed the fly ash and cement in the amount of absorbed moisture at the initial stage, but then the increment in their weight becomes much less than in the fly ash and cement. Moreover, the curves of the experimental mixes are arranged in order of increasing fly ash content. Cement in this case occupies a special position since in addition to physical adsorption it enters into chemical interaction with water.

3.3. Compressive strength test results and flexural strength test results

The test results are presented in Figure 5 and Figure 6. The figure shows that, despite the expanding effect, “Zolest-bet” oil shale fly ash increases the compressive strength of concrete as compared to the control mix No. 6 in case reducing cement and fly ash content. If the fly ash content is 30% by weight of cement (mix No. 4), then the compressive strength is higher than if the fly ash content is 40% by weight of cement (mix No. 5) for all concrete hardening periods. The authors suggest that this is due to the expansion factor. Therefore, it is necessary to find the optimum fly ash content in strength when designing concrete.

At the same time, the flexural strength of mixes containing the fly ash turned out to be lower than the flexural strength of the control mix No. 6 in the initial period of up to 15-22 days (Figure 6). Mix No. 4 and mix No. 5 with fly ash overtook the control mix No. 6, by 24 and 17%, respectively, in the subsequent periods. Here also, the mix with a lower fly ash content showed a higher flexural strength at all hardening periods.
3.4. Heat release dependence on fly ash “Zolest-bet” content

The change in the rate of heat release for the mix No. 7 with the replacement of 20% cement by fly ash and the control mix No. 8 without fly ash is shown in Figure 7.

![Heat release dependence on fly ash “Zolest-bet” content.](image)

The heat release rate of the control mix No. 8 significantly exceeds the heat release rate of the mix No. 7 at the initial stage up to 1 day. Also, the control mix No. 8 gives a higher and sharper peak of exotherm, ahead of the peak for the mix No. 7. The fly ash addition provides a calmer, extended in time heat release with low self-heating of concrete in the initial period from 1 to 3 days. That is especially valuable for the thermal crack resistance of concrete.

4. Conclusions

Experimental studies on the influence of oil shale fly ash additives “Zolest-bet” on thermal expansion, strength, shrinkage, and heat release of concrete were carried out. The results obtained lead to the following conclusions:

1. The addition of 30% fly ash over cement content increases the thermal expansion by 6 times. The addition of 40% fly ash increases the thermal expansion by 16 times. On the one hand, the expansion is due to the high free calcium oxide content (10%) in the fly ash. On the other hand, that is due to the high sulfuric acid anhydrite SO₃ content (10.3%). It forms a highly expanding calcium hydrosulfoaluminate upon reaction with tricalcium aluminate cement in an unlimited amount of water.

   There is a rapid growth of expansion in the initial site (up to 20 days). Then the process slows down and practically stops after 40 days, having reached the expansion limit. Upon reaching 90 days, the opposite process begins – shrinkage. This process is difficult to explain within the framework of this work. The only thing that can be said is that shrinkage is associated with the presence of oil shale fly ash. Since if there is no fly ash, then there is no shrinkage.

2. The oil shale fly ash addition over cement content significantly reduces shrinkage. If the ash content is higher, then the shrinkage decreases more. Shrinkage is on average 1.3 times less at a 30% fly ash content, and shrinkage is 1.8 times less at a 40% fly ash content. The shrinkage decrease occurs due to the expanding effect of fly ash. The predominant effect of shrinkage ends by the 30-day period. After that, the expansion can exceed the shrinkage. There is an alternate change in the sign of the deformation. This may be due to fluctuations in air humidity and a change in the sorption humidity of the samples. Thus, increasing the concrete moisture and the connection of additional moisture to the calcium hydrosulfoaluminate leads to an increase in its volume. When additional moisture is bound by hydrosulfoaluminate, the predominance of shrinkage over expansion begins.

3. It has been experimentally shown that fly ash has a higher sorption capacity than cement. Samples with the oil shale fly ash addition absorb more moisture than mixes without fly ash.
4. Despite the expanding effect, “Zolest-bet” oil shale fly ash increases the compressive strength. If the fly ash content is 30% by weight of cement, then the compressive strength is higher than if the fly ash content is 40% by weight of cement for all concrete hardening periods. Therefore, there is an optimum fly ash content in terms of strength.

At the same time, the flexural strength of mixes containing the fly ash turned out to be lower than the flexural strength of the mix without fly ash in the initial period of up to 15-22 days. Mixes with fly ash content in the amount of 30% and 40% by weight of cement exceeded the flexural strength of the mix without fly ash, respectively, by 24 and 17%. Here also, the mix with a lower fly ash content showed a higher flexural strength at all hardening periods.

5. The heat release rate of the mix without fly ash significantly exceeds the heat release rate of the mix with fly ash at the initial stage up to 1 day. Also, the mix without fly ash gives a higher and sharper peak of exotherm, ahead of the peak for the mix with fly ash. The fly ash addition provides a calmer, extended in time heat release with low self-heating of concrete in the initial period from 1 to 3 days. That is especially valuable for the thermal crack resistance of concrete.

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