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COMPOSITION AND PROPERTIES OF OIL SHALE ASH CONCRETE

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Abstract. *Oil shale ash (OSA) as a binder has air, pozzolanic or latent hydraulic properties depending on the combustion temperature and type of ash collection equipment. This paper focuses on the use of OSA as the main binder for low strength concrete. Impact of hardening conditions on the strength development and soundness of various concrete mixes made with two main types of OSA and their mixes was tested. Crushed limestone was used as aggregate. Concrete mixes were designed at an OSA:aggregate ratio of 3:1 and 1:1, using fresh concretes with the same workability. The results revealed differences in the strength development, 28-day compressive strength and durability properties between hardened concretes made with various OSA binders. The compressive strength of concretes made with various OSA was tested in different curing conditions. The durability properties of OSA based hardened concrete such as water absorption and resistance were tested. The results of expansion and water resistance tests indicated that by increasing the content of CFB ash in OSA binders, water resistance was improved and expansion diminished.*

Keywords: *concrete, oil shale ash, strength, durability, pozzolanic properties, hydraulic properties.*

1. Introduction

The majority of mined oil shale is utilized as solid fuel in thermal power plants for electricity and heat production and about one fifth of oil shale is used for retorting shale. Estonian oil shale is characterized by its high content of carbonate minerals [1]. The total amount of OSA formed is about 50% of the fuel mass. Oil shale ash is formed from solid fuel mineral matter in the amount which depends on the combustion temperature and other conditions. Besides the release of free oxides in the combustion process, the decomposition of oil shale causes the formation of new chemical compounds. The type and amount of these compounds depend directly on the

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characteristics of the combustion process. In spite of the long-term research of reusability options, most of OSA is still deposited in ash sediment fields next to the power plants. Deposits of OSA cause serious landscape modifications in the area surrounding the power plants which use oil shale as fuel [2]. In the atmospheric conditions a number of transformations take place, including carbonation of free CaO, hydration of calcium silicates, calcium aluminates and calcium ferrites, which provoke hardening and ash stone formation at deposits [3].

Part of the formed OSA is collected and utilized as dry material. Various types of OSA have properties of a mineral binder, the hydration type of which varies from air hardening (coarse bottom and cyclone OSA types) to pozzolanic (CFB OSA) and latent hydraulic (PF OSA). Estonia has more than a fifty-year practice of using OSA from the electrostatic precipitator of high temperature (about 1400 °C) pulverized fuel (PF) boilers as the second main constituent of Portland cement [4, 5]. Coarse cyclone ashes with a high content of free CaO (CaO_{free}) have been utilized as lime substitute in the building materials industry, for pavements construction or in agriculture.

Type of hardening depends on the chemical and mineral composition of OSA, which in turn depend on the combustion temperature: 800 °C at low temperature fluidized bed combustion (CFB) and 1400 °C at high temperature pulverized fuel combustion (PF). At its larger amount of free SiO_2, or lower ratio of $(CaO+Al_2O_3+Fe_2O_3):SiO_2$, the binding properties of CFB OSA are approaching pozzolanic, unlike PF OSA's. Results of our previous tests [6] showed that the amount of CaO bound by CFB OSA in a saturated lime solution was about twice higher than the PF OSA bound CaO amount. Type of hydration has a direct impact on the building properties of OSA based concrete. Water demand of CFB OSA constituent was substantially higher [7], which is typical of pozzolanas [8]. Concrete made with Portland cement containing high temperature OSA as the second main constituent revealed higher water absorption, lower sensitivity to alternate wetting-drying and decreased water resistance [7].

In this paper, the results of tests with mixed PF and CFB ashes as binders for ash concrete mixes, which had been caught by different dust systems, are analyzed. In the designed concrete mixes, OSA was found to act as the main binder. In the current work, the compositions and constituents available in Estonia are proposed for producing oil shale ash concrete to be used for backfilling or as road base material. To determine the role of a given type of OSA as the main binder in concrete, efforts were made to characterize the micro- and macrostructural properties of the concrete produced. Physical properties of total OSA mix, such as particle shape and size distribution, are of essential importance regarding aggregate-ash paste interface characteristics, fresh ash concrete workability or packing efficiency and, consequently, the durability of hardened concrete.

Using OSA as the main binder in the concrete depends on the strength, porosity and durability characteristics developed. According to Neville [9], low porosity, water penetration and vapour and gas permeability are important to protect concrete against various deterioration mechanisms. The durability of concrete depends largely on the ease of migration of fluids in liquid or gaseous form through the hardened concrete mass. They can move through the concrete in different ways, but the ease of transport depends primarily on the structure of the hydrated paste.

To utilize total dry OSA as concrete for backfilling or road basement will require working out mixes of OSA, which would be able to harden concrete and make it durable in exposure conditions [10]. Low temperature and presumptive contact with water in the early period of hardening are challenges for OSA concrete to meet. The ratio of CFB OSA to PF OSA has a conclusive impact on the soundness and volume changes of hardened concrete (Fig. 1). To achieve the optimal expansion of the backfilling concrete mass, the CBF ash to PF ash ratio in OSA should be regulated.

The authors' approach is that the simplest and most economical method in practice would be to utilize total OSA, without separation by combustion regime, particle size, content of CaO_{free}, etc.

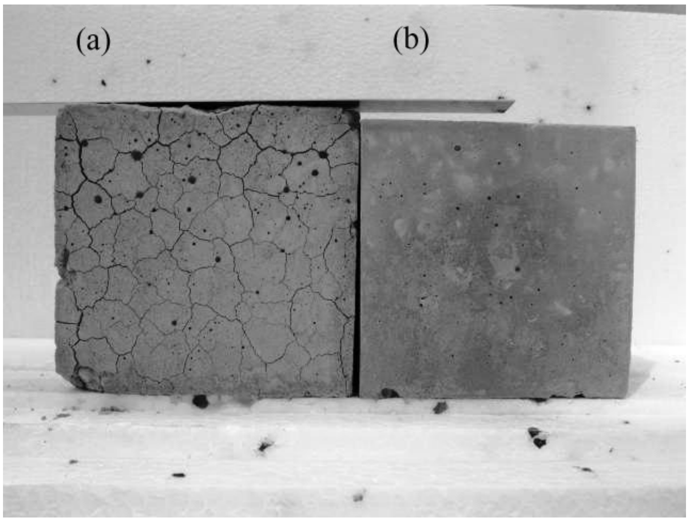

Fig. 1. Expansion and cracking of hardened concretes made with PF OSA (a) and 50% PF OSA + 50% CFB OSA (b).

2. Materials and methods tested

Various OSA with different portions of high (PF) and low (CFB) temperature burnt ashes and their mixes were used as the main binder for low compressive strength ash concrete, using the mining residue – crushed limestone – as an aggregate.

Characteristics of OSA and the aggregate were analyzed using EN 196 and EVS-EN 1744 [11] methods (Table 1). Particle size distribution was determined by sieving.

Table 1. Characteristics of tested OSA

OSA	CaO_{free}, %	CO_2, %
PF	17.5	2.1
CFB	6.6	12.5

The total PF OSA used consists of separately collected bottom ash (about 40%) and fly ash. CFB OSA was also total ash from the ash field. Both binders contained OSA particles > 2 mm in size. For paste and mortar tests the coarse material comprising also > 2 mm particles was crushed until it passed a 2 mm sieve and was mixed.

Table 1 shows substantial differences in parameters, such as content of CaO_{free} and undecomposed $CaCO_3$, as influenced by different combustion temperatures. Loss on ignition was tested with material dried at 105 °C, afterwards heated to 975 °C and CO_2 content was calculated. The test results reveal the CO_2 content to be about 12.5% by mass of CFB OSA. The tested ashes do not conform to the requirements for fly ash used in Portland cement concrete as specified in EN 450-1 [12]. Excluding specific surface area, the basic properties of the tested CFB OSA meet the requirements for burnt oil shale set in EVS 636:2002 [13]. In spite of the conformity, the binding properties of various OSA as an independent mineral binder vary to a large extent.

The standard EVS-EN 450-1 specifies requirements for fly ash used in concrete, limiting the content of CaO_{free} to less than 2.5%. If the CaO_{free} content in fly ash rises above 2.5%, conformity with the requirements for soundness should be tested.

The aim of the present work was to find possibilities for utilization of oil shale ashes other than the second main constituent of Portland cement. The described methods were used to elucidate the influence of OSA type and properties on the produced ash concrete. Research was focused on the elaboration of OSA concrete by testing OSA based pastes, mortars and concretes.

Various OSA compositions (Table 2) were tested according to EN 196 to determine water demand and setting time (Fig. 2). Ash mortars (ash to sand ratio 1:3 by weight and water to cement ratio 0.50) were made by EN 196-1, using CEN standard sand. The specimens were cured in water at a relative humidity (RH) of 95 ± 5% and temperature 20 ± 1 °C until testing. Le Chatelier´s expansion tests were carried out with mortars consisting of OSA and fine aggregate (EN standard sand).

Table 2. Composition of OSA binders

No.	OSA	Composition of binder, %	
		PF OSA	CFB OSA
I	80 PF + 20 CFB	80	20
II	20 PF + 80 CFB	20	80
III	50 PF +50 CFB	50	50
IV	CFB	0	100
V	PF	100	0

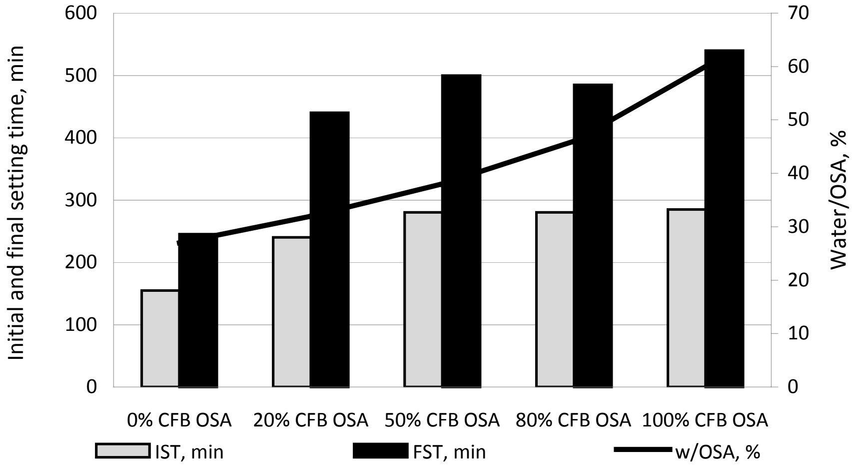

Fig. 2. Initial (IST) and final (FST) setting time and water demand of OSA pastes depending on CFB and PF ashes percentage in OSA.

Pastes were made with standard consistency (Table 3) and hardened in a Le Chatelier mould for three days at 20 ± 1 °C and 95 ± 5% RH. Further hardening continued for 28 days in water and at 95 ± 5% RH and 20 ± 1 °C. Some specimens were boiled. Expansion was measured between the wires of the mould. Figures 3 and 4 illustrate the results of soundness tests.

Table 3. Water demand of tested OSA binders

OSA binder specification	Composition, %		Water demand of OSA paste, (water/OSA), %
	OSA	Aggregate	
PF OSA	100	0	27
CFB OSA	100	0	60
80 PF + 20 CFB	100	0	32
50 PF + 50 CFB	100	0	38
20 PF + 80 CFB	100	0	46

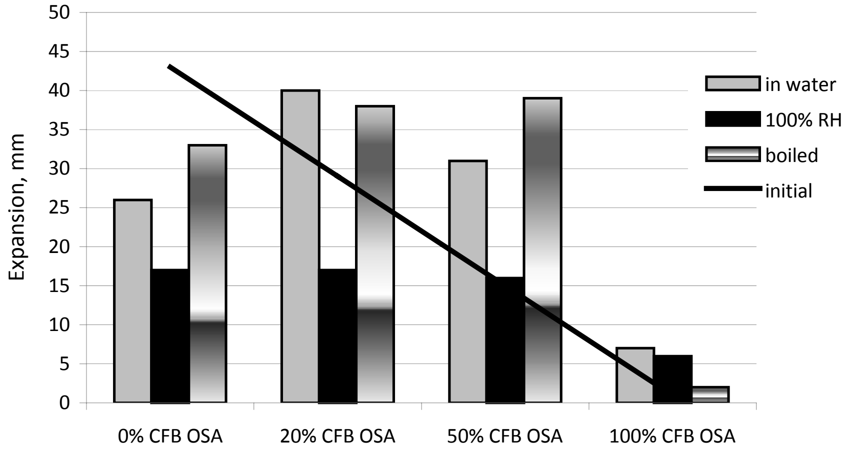

Fig. 3. Expansion of pastes made with OSA binders after three days of initial hardening at 20 ± 2 °C (line) depending of CFB and PF ashes percentage in OSA.

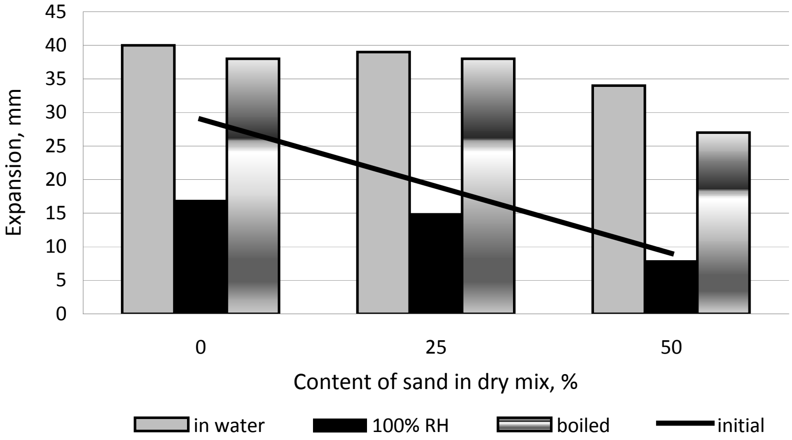

Fig. 4. Expansion of mortars made with OSA binder (50% CFB OSA + 50% PF OSA) made with various sand contents (initial expansion measured after a three-day hardening at 95 ± 5% relative humidity).

Fresh ash concretes with the same workability were made at an OSA:aggregate ratio of 1:1 and 3:1 (dry mass), using a 0–16 mm crushed limestone fraction as an aggregate.

The OSA:aggregate proportions in concrete mix were established on the basis of small trial batches to verify the target slump of 100 to 150 mm. Target slumps were maintained with water:cement ratios allowed to vary.

All ash concrete mixtures were mixed in a concrete mixer, following the procedures recommended in EN 480-1 [14]. Specimens were cast in cubical moulds with dimensions of 150 × 150 × 150 mm and 100 × 100 × 100 mm. The fresh mixes were compacted by vibration (5–7 s on a vibrating table). The prisms were demoulded after a 48-hour hardening. Further curing followed in standard conditions until testing. The strength of ash concrete was measured at the ages of 2, 7, 28 and 91 days. The depth of penetration of water under pressure was tested using the EN 12390-8 [15] method, except that the applied pressure was 200 ± 50 kPa. 150 × 150 × 150 mm cubic concrete specimens of the age of 28 days were placed in the water impermeability tester and water pressure was applied. The specimens were split in half perpendicularly to the face on which the water pressure was applied and the depth of penetration of the waterfront was measured.

3. Discussion

The decreased firing temperature of about 800 °C used in fluidized bed (CFB) boilers increases the content of undecomposed material in OSA. At the same time, the formation of melted glassy cover on the OSA particle surface was hindered, the content of minerals decreased and that of free SiO_2 increased, differently from the case with high temperature PF OSA [6]. Figure 2 shows the changes in properties evoked by the particular type of OSA in binder mixes. The increase of CFB OSA in the binder from 0% up to 100% is accompanied by the increase of water demand and setting times. The increased content of CFB OSA in the binder implies an increased water demand of the concrete mix as a result. In the case of CFB OSA, the pozzolanic hydration process proceeds with a longer initial setting time. If the CFB OSA content in the binder exceeds 50%, this is not so obvious. The increase of the CFB constituent in the binder increases water demand.

The expansion of specimens was measured after 28 days of storage in water, at 95% RH and one third of specimens was boiled and measured after the initial three days of hardening (Figs. 3 and 4). Most of the tested OSA, especially high temperature PF OSA, does not meet the requirements of EVS-EN 450-1 for fly ashes for concrete. The reason is often the increased expansion caused by the high CaO_{free} content. Usually CFB OSA is characterized by a decreased content of CaO_{free}, unlike PF OSA. The tested total OSA includes coarse fractions of CBF and PF ashes, which provoke heterogeneous expansion.

The results of Le Chatelier's tests presented in Figure 3 show differences in expansion influenced by various test conditions. Storage in water or boiling of hardened OSA paste cylinders causes higher expansion compared to storing in high humidity conditions. The initial expansion of specimens depends on the CFB OSA content in the binder, the increase of which leads to the decrease of expansion. At 100% CFB OSA as binder, the expansion does not exceed 10 mm, despite the storage conditions used. High temperature PF OSA specimens (0% CBF OSA) have the highest initial expansion during three days of hardening at 100% RH.

Figure 4 illustrates the impact of aggregate content in the mortar on the expansion and soundness of hardened specimens made with OSA. The extensive expansion and cracking of mortars made with 50% CFB OSA + 50% PF OSA at boiling or in water decreases the durability of hardened OSA concrete. Production of sound OSA mortar or concrete is possible at a CFB OSA content of 50% or more in the binder and the aggregate content of higher than 50% in the dry mix mass.

In exceptional circumstances (for specific purposes for backfilling with OSA concrete), some volumetric expansion without cracking may be eligible. The results verify that by modifying the CFB:PF ashes ratio in the binder, the expected expansion value can be obtained.

The strength of OSA binders was tested using OSA mortar and concrete specimens made with fine or coarse aggregate in OSA:aggregate proportions of 1:3, 3:1 or 1:1 and under different hardening conditions.

Hardened mortars (1:3) made with a CFB OSA content of 80–100% exhibit the highest compressive strength, in spite of high water demand (Table 4). The decrease of CFB OSA content in the binder decreases the strength of hardened mortar.

Use of total OSA as a binder raises issues caused by differences in the main properties between various OSA types gathered from different dust collectors. Bottom and cyclone ashes greatly differ in particle size, amount of > 1 mm particles, specific surface area and CaO_{free} content (Table 1). The hydration process depends directly on the particle size of the binder. The increased content of CaO_{free} causes expansion and leads to the cracking of hardened concrete.

Tests were carried out with concretes made with a binder consisting of total CFB OSA and PF OSA. The aggregate content of concrete mixes was 25% and 50% by mass (mixes 3:1 and 1:1, respectively) (Fig. 5). Concretes were hardened at 95 ± 5% RH and temperatures 20 °C and 5 °C (Fig. 6). After 28 days of hardening the compressive strength of 100% PF OSA concrete at 20 °C was 2–2.4 N/mm^2. The compressive strength of 100% PF OSA concrete hardened for 91 days at 20 °C increased twofold compared to

Table 4. Strength properties of 4 × 4 × 16 cm prisms made with 1:3 mortars of OSA:sand (EN 196) (compressive strength determined after 28 days of hardening)

Type of OSA	Water/OSA ratio	Compressive strength, N/mm^2
100 CFB	0.8	3.9
100 PF	0.5	2.1
80 PF + 20 CFB	0.5	1.9
50 PF + 50 CFB	0.5	1.9
80 CFB + 20 PF	0.8	4.6

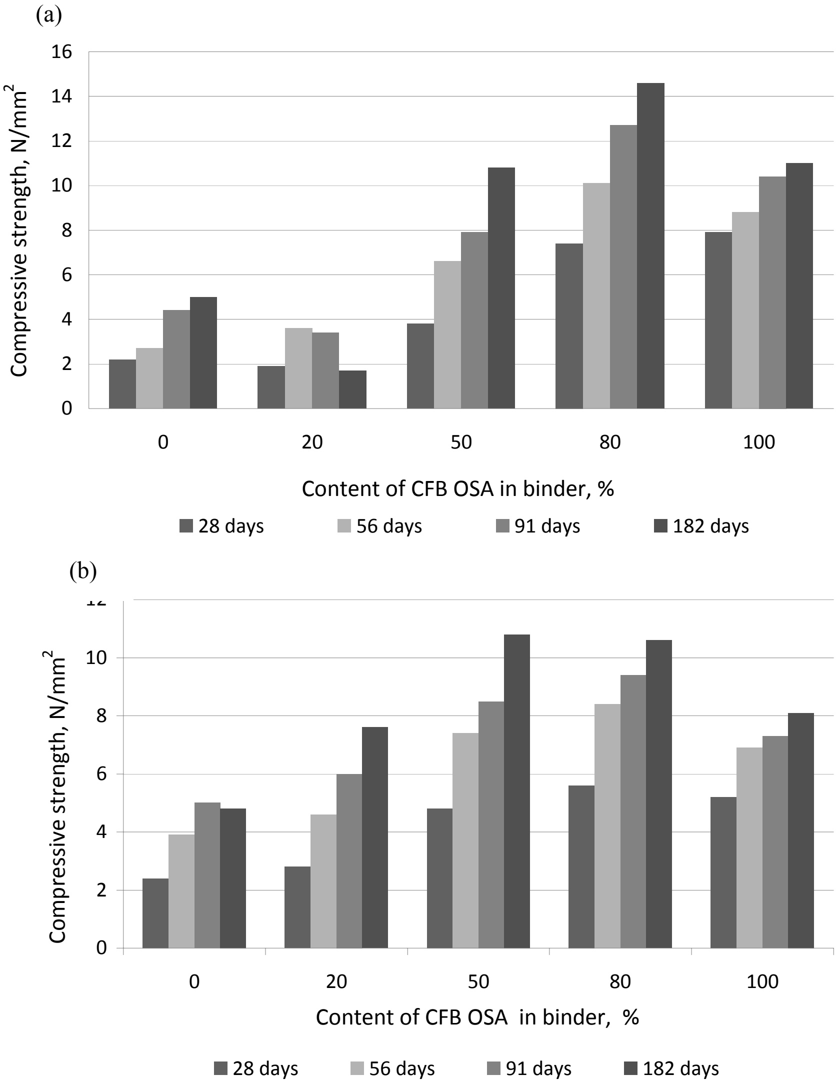

Fig. 5. Compressive strength of OSA concretes made with 3:1 (a) and 1:1 (b) OSA:aggregate, hardened at 95 ± 5% RH and 20 °C.

that of concrete hardened for 28 days, reaching 2–4 N/mm^2. At 182 days the compressive strength was about 5 N/mm^2. The compressive strength of OSA concrete (3:1) hardened for 28 days at 20 °C exceeded 7.9 N/mm^2 at 100% CFB OSA. Further hardening for 182 days led to an increase of compressive strength, especially with binders with 50 and 80% CFB OSA. Increasing the CFB OSA content in concrete to 100%, the compressive strength was reduced (Fig. 5). Concretes with an OSA:aggregate ratio of 3:1 showed a higher compressive strength than 1:1 concretes.

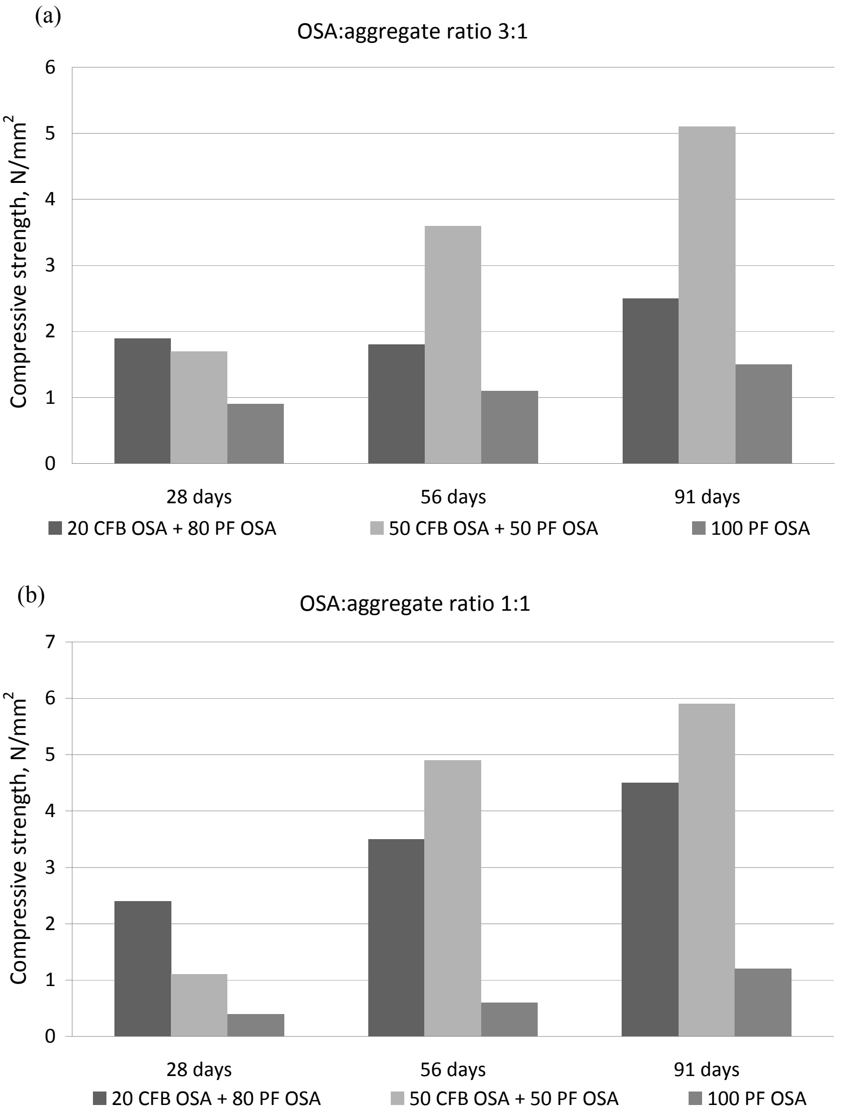

Fig. 6. Compressive strength of OSA concretes 3:1 (a) and 1:1 (b) hardened at 95 ± 5% RH and 5 °C.

Use of binder with a PF OSA content of 80–100% led to decreased strength values. The main obstacles derived from expansion (Fig. 1) were caused by the high CaO_{free} content in the total PF OSA used. When increasing the aggregate content in the mix, expansion diminished. The high content of CaO_{free} and heterogeneous particle size of PF OSA were due to coarse bottom and cyclone ashes included in it (Figs. 3 and 4). Use of OSA as an independent binder for low strength concretes is perspective at the CFB OSA portion in the binder between 20 and 80%.

The continuous increase of strength at later hardening ages depended on the PF OSA constituent: regulated expansion without cracking may be achieved by excluding the coarse types of OSA (bottom and cyclone ashes).

Strength growth depends directly on temperature and humidity conditions. Therefore, strength development at 5 °C was tested. Figure 6 shows test results of concretes made with three OSA binders. Low hardening temperature causes a decrease in compressive strength.

Concrete composed of 50% CFB OSA and 50% PF OSA has the highest compressive strength at 5 °C. The compressive strength of concrete hardened for 28 days is 1.7 MPa (ratio 6:1; Fig. 6a), being at 20 °C twice higher, 3.8 MPa (ratio 3:1; Fig. 7). During further hardening concrete made with a higher aggregate content (1:1) has a higher strength.

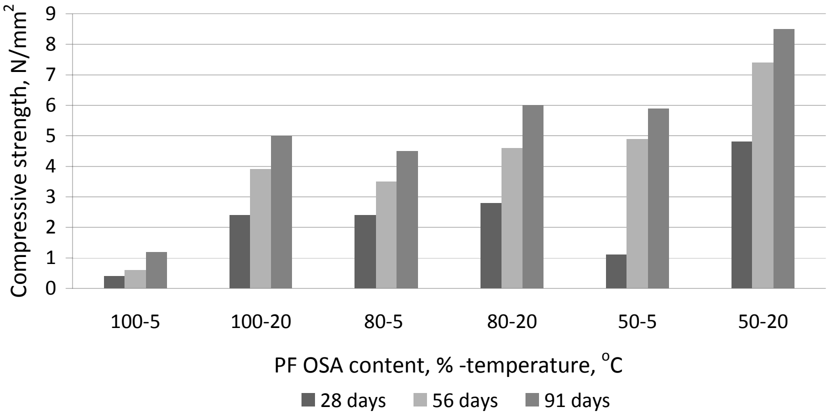

Fig. 7. Compressive strength of OSA concretes 1:1 hardened at 95 ± 5% RH and 5 °C (marked as 100-5, 80-5 and 50-5) and 20 °C (marked as 100-20, 80-20 and 50-20).

The 28-day compressive strength of concrete made with PF OSA and CFB OSA (80:20 by mass) was less sensitive to hardening temperature (columns 80–20 and 80–5, Fig. 7).

Concrete made with 100% PF OSA and hardened at 5 °C had the lowest strength and highest sensitivity to hardening temperatures (Figs. 5, 6, 7). Addition of CFB OSA increased the compressive strength of OSA concretes at later ages of hardening at low temperatures.

The density of OSA concretes hardened for 28 days was between 1700 and 1800 kg/m^3. The decrease of OSA content in the concrete mix increased its density.

A visual inspection of hardened concrete cubes (20% CFB OSA + 80% PF OSA) reveals external cracking, in spite of solid and sound internal structure. Cubes made with 20% CFB OSA and 80% PF OSA have visible cracks. The decrease of expansion occurred at a low hardening temperature, 5 °C, unlike 20 °C.

Durability of OSA concrete is directly influenced by exposition and climate conditions. Various OSA concretes were tested for water absorption and depth of water penetration to evaluate their durability (Fig. 8). The tests were carried out 28 and 182 days after curing.

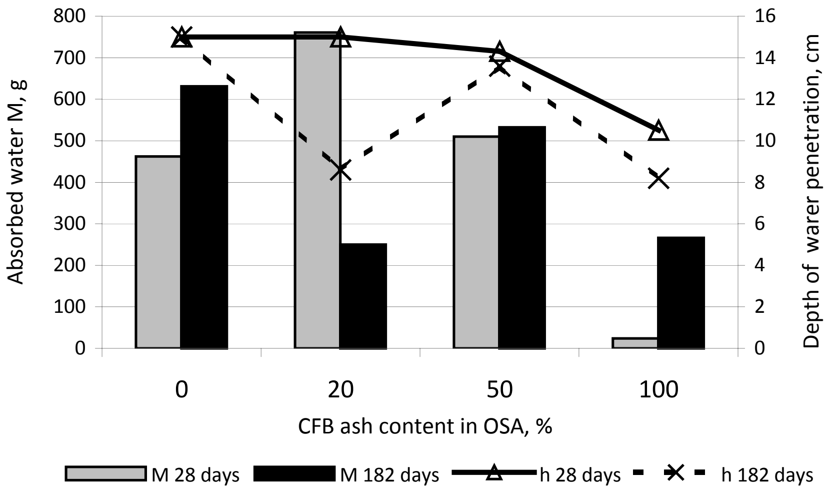

Fig. 8. Water resistance of 1:1 OSA:aggregate concrete determined at pressure of 200 kPa (EVS-EN 12390-8).

The depth of water penetration was the lowest at 100% CFB OSA after curing for 28 days. CFB OSA improved concrete's resistance to water (Fig. 8). Concretes showed changes in water absorption at various curing ages, which agrees with findings of Hearn et al. [16] and Wang and Ueda [17]. Water penetration and absorption in mostly PF OSA concretes was high. With increasing CFB OSA content the penetration of water in concretes cured for 28 days diminished. After 182 days of hardening, water absorption and depth of water penetration in 100% CFB OSA concretes were the lowest. According to Wang and Ueda [17], the continual hydration process causes changes in pore size distribution and water absorption, concurrently. The mutual relationship between pozzolanic (CBF OSA) and latent hydraulic (PF OSA) properties of the used OSA mixes causes temporal variations in concrete structure formation. In spite of the lower testing pressure (200 instead of 500 kPa) applied, the tested OSA concretes do not meet requirements for water resistance for Portland cement concrete. The successful utilization of OSA concretes for filling purposes will be possible only after performing further long-term durability tests.

4. Conclusions

The compressive strength and strength development of OSA concretes made with the CFB ash at a content of 20–80% and limestone mining residue as aggregate are sufficient to utilize them for filling purposes.

The decrease in concrete strength growth occurring at low curing temperatures may be compensated by the increased CFB ash portion in OSA.

The expected values of compressive strength, expansion and durability characteristics of OSA concrete can be determined by changing the PF ash to CFB ash ratio in the OSA binder.

The water resistance of OSA concrete is not comparable with that of Portland cement concrete. Water resistance can be improved by increasing the CFB ash portion in the binder.

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