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DURABILITY BEHAVIOR OF PORTLAND BURNT OIL SHALE CEMENT CONCRETE

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Combustion temperature of oil shale in pulverized fuel boilers and in fluidized bed combustion equipment is different. High temperature burnt oil shale from pulverized combustion boilers and low temperature burnt oil shale from a CFB (Circulating Fluidized Bed) boiler differ in their mineral composition and surface properties of ash particles. Variations in the properties of ashes affect hydraulic properties of burnt oil shale as a binder or as the main constituent of Portland cement. Differences in the frost resistance of concretes made with various second main constituents show how significant is the type of hydration of the second main constituent in terms of the durability. Alternate immersion-drying tests were carried out to analyze the frost resistance of concretes compared to the other main constituents.

The objective of this work was to investigate the influence of various burnt oil shales as the main constituent of Portland cement on the durability of concrete compared to the main constituent such as pulverized limestone.

Introduction

Durability of Portland cement concrete is in direct dependence on capillary pore structure and volume of cement stone in contact with water. The volume and size of capillary porosity of Portland cement stone depends on the mixing water content as well as on the type of Portland cement.

Today instead of Portland cement clinker, other constituents are commonly used. This is one of the possibilities to minimize consumption of natural raw materials and energy. Other main constituents of Portland cements listed in EVS-EN 197-1 (Estonian standard) usually increase water demand. Portland cement standard EVS-EN 197-1 does not incorporate direct water demand limits for different concretes. Portland cements with various other main constituents specified in EVS-EN 197-1 conform to the requirements of European standard.

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Other main constituents may be divided by the type of hydration process into inert, pozzolanic and hydraulic constituents. Cements with various main constituents have different durability properties, which have been specified. This leads to durability issues caused by various climatic and environmental conditions.

Focus in this paper is on durability issues of concretes made with cements consisting of different types of main constituents listed above. Water permeability and capillary water content, alternate immersion-drying in various solutions, sulphate and frost resistance of concrete are characteristic properties of durability.

According to the EU standard, the allowed content of limestone as the constituent of common Portland cement is up to 35%. Many published papers have reported poor durability behavior of Portland limestone cements containing limestone more than 5%. According to R. G. Hooton and M. D. A. Thomas [1], concretes produced with cements containing C_3A 5.3–13.1% and limestone 5–25% had no consistent differences when exposed to Na_2SO_4 (1.5% SO_3) and $MgSO_4$ (0.35 and 1.5% SO_3) solutions. At the same time, cements with high content of C_3A and 25% of limestone had poor sulphate resistance. Research results of S. T. Lee et al. [2] and K. Tosun et al. [3] show a decrease in corrosion resistance caused by sulphate and magnesium solutions of concretes made with Portland cements containing 10–40% of limestone.

According to S. Tsivilis et al. [4] concretes, which contain limestone cement up to 20% show lower resistance to freezing and thawing than the concretes made from common cement.

Another aspect of durability is an increased intensity of rebar corrosion due to increased permeability and capillary water absorption of concrete caused by the second main constituent. Authors have found that the Portland limestone cement, with limestone content up to 20%, shows protective properties against rebar corrosion [4]. The same authors refer to lower permeability and higher water absorption properties of Portland cement containing limestone up to 20%. Consequently, porosity of concrete made with Portland cement containing limestone more than 15%, increases [5].

Limestone is acting mostly as an inert constituent. Some authors [6] describe thaumasite as hydration product of Portland cement clinker minerals and limestone constituents.

According to N. Voglis et al. [6], Portland limestone cement (15% L) has higher early strength and XRD patterns show a peak of $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ after 24 hours, increasing up to 28 days of hardening. T. Matschei et al. [7] report shows that calcite affects the content of free $Ca(OH)_2$ and the balance of AFm and AFt phases. Space filling ability of calcite maximizes the AFt content in the cement stone. It is found that calcite performs two functions: less than 5% of calcite might be reactive with cement and the rest of it is inert. The role of thaumasite in the durability of concrete is not perspicuous.

The aim of the present research is to compare frost and alternate immersion resistances of concretes made from Portland limestone cement and Portland-burnt oil shale cement as the second main constituents, and study the influence of alternate immersion-drying and freezing-thawing on the structure of concrete.

Both limestone (L) and burnt oil shale (T_T) are used as traditional second main constituents of Portland cement. Fine grounded limestone has properties of an inert material and almost does not participate in the hydration process [6, 7].

Oil shale is the main fuel used in Estonian power plants. Depending on the combustion temperature, burnt oil shale is generally characterized as a hydraulic or pozzolanic constituent. The combustion process of solid fuels differs in combustion temperatures in the boiler, fuel type and the ash collectors used. A high temperature (>1300 ^oC) combustion process of oil shale produces spherical particles with a smooth vitrified surface (T_T). Some reconstructed boilers have lower combustion temperature of 800 ^oC. It means that variations in the shape, surface and the chemical-mineral composition of the burnt oil shale (T_K) are formed [8].

Various types of burnt oil shale, T_T and T_K as the second main constituents, have substantial differences in the hydration process. A low temperature burnt oil shale (<800 ^oC) T_K is characterized by higher water demand compared to the high temperature burnt oil shale (>1300 ^oC) T_T. This means that with an increasing water demand of Portland cement the strength of concrete decreases. Consequently, the pumping-grade of fresh concrete is improved by the increase of water content and the amount of capillary pores increases.

Our previous test results have confirmed [8] that the high temperature burnt oil shale T_T (combustion at >1300 ^oC) has a higher content of minerals such as belite and monocalcium aluminate. T_T consists of a vitreous phase mainly of calcium aluminates and ferrites. Compared to T_K the high temperature burnt oil shale contains less insoluble residue, mainly amorphous SiO_2. This composition provides reference conditions for the hydraulic binding process. Preceding tests have shown [8, 9, 10] that the low temperature (800 ^oC) burnt oil shale T_K has lower content of minerals and a higher content of free oxides compared to the high temperature burnt oil shale T_T. Consequently, the hydration type of the low temperature burnt oil shale T_K is mostly pozzolanic.

Density and capillary pore structure of concretes made with various Portland cements vary in a wide range, resulting in differences in water absorption, alternate wetting-drying and frost resistance. These properties and their changes are of essential importance in wet and cold climate conditions.

Experimental and discussion

The aim of planned tests was to find out reasons causing variations in the frost resistance of concretes made with Portland cements with an inert, hydraulic or pozzolanic hydration type of the second main constituent. The list of Portland cements tested is given in Table.

Table. **Composition of tested Portland cements**

	Portland cement	Composition of Portland cement, %		
		Limestone L	Burnt shale T_T	Burnt shale T_K
1	CEM I	0	0	0
2	CEM I /5L	5	0	0
3	CEM II/A-10L	10	0	0
4	CEM II/A-15L	15	0	0
5	CEM II/A- 20L	20	0	0
6	CEM II/A-18T_T	0	18	0
7	CEM II/A-15 T_K	0	0	15
8	CEM II/A-20T_K	0	0	20
9	CEM II/B-25T_K	0	0	25
10	CEM V/B(15T_K+10L)	10	0	15

Limestone content (L) of Portland cements varied from 0 up to 20%. Besides the limestone the hydraulic high temperature burnt oil shale T_T and the pozzolanic low temperature burnt oil shale T_K were used.

Fresh concretes with the same workability were made with Portland cement (320 kg/m^3) using limestone as a coarse aggregate. Hardening of concrete cubes took place at 95±5% relative humidity at 20 ^oC.

Frost resistance was tested by the EVS-814 method. This method indicates external structural damage and is based on determination of loss from the surface of concrete (scaling). Water-saturated specimen, covered with 3 mm of distilled water or NaCl solution, was exposed to alternate freezing and thawing.

Freezing temperature was –25±2 ^oC. After freezing cycle thawing in the water at +20 ^oC was conducted. After 7, 14, 28, 42 and 56 cycles the mass loss of the scaled material was determined.

Changes in mass after alternate immersion-drying were tested with mortar specimens hardened for 28 days. After 24 hours of immersion in the tap water with a temperature of 20 ^oC specimens were dried at 100 ^oC. After every cycle the absorbed water content and mass changes were determined and calculated.

The depth of water penetration was tested under 500 kPa pressure by the EN 12390-8 method.

Freezing resistance of various concrete compositions depends on the properties of the coarse aggregate (Fig. 1). Granite has low water absorption up to 0.5% while limestone has water absorption of about 2% and more.

Consequently, limestone aggregate has a decreasing effect on frost resistance of concrete. Fig. 1 illustrates the comparison of the total loss of scaled mass made with limestone (L) and granite (G) as coarse aggregates. High water absorption of limestone aggregate causes an obvious decrease in the frost resistance, despite of the cement used. Concurrently, the depth of water penetration under pressure showed an increase of 15 up to 21 mm with limestone aggregate as compared to that of granite.

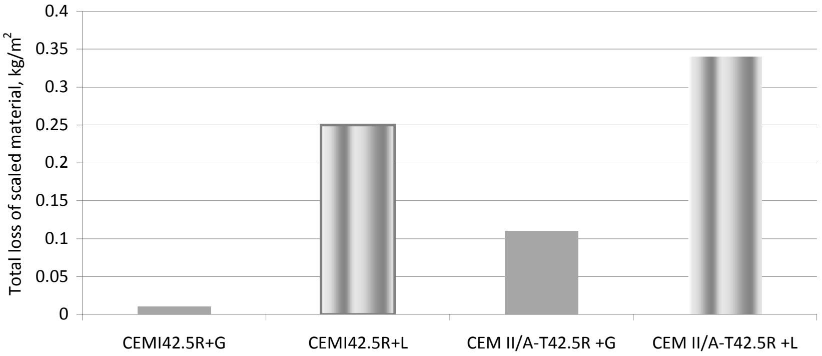

Fig. 1. Frost resistance of concrete made with various coarse aggregates. Limestone (L); granite (G).

Authors assume that analogical situation occurs in case of an inert second main constituent, i.e. limestone, as a constituent of Portland cement.

Pozzolanic type of hydration involves a reaction between the reactive SiO_2 of the second main constituent T_K and $Ca(OH)_2$ initiated by the hydration of clinker minerals. The extra amount of generated calcium hydrosilicates has a decreasing impact on the capillary diameter and reduces the water penetration of the concrete. Reports about the sensitivity of wetting-drying or frost resistance of concrete made with pozzolana are different.

Differences in the frost resistance of concretes made with various second main constituents show how significant is the type of hydration of the second main constituent in terms of the durability. Alternate immersion-drying tests were carried out to analyze frost resistance. The aim was to show the impact of an inert (L) or pozzolanic (T_K) type of constituent on the water absorption and possible structure damages of concrete in contrast with the hydraulic constituent T_T.

Pulverized limestone (up to 15%) was used as the second main constituent in concretes and the frost resistance to alternate freezing and thawing was tested in distilled water and in deicing salt solution. Results presented in Fig. 2 show low frost resistance of all tested concretes. Increasing the limestone content of the cement from 5 up to 15% had a light decreasing effect on frost resistance in these circumstances. The loss of scaled material in case of

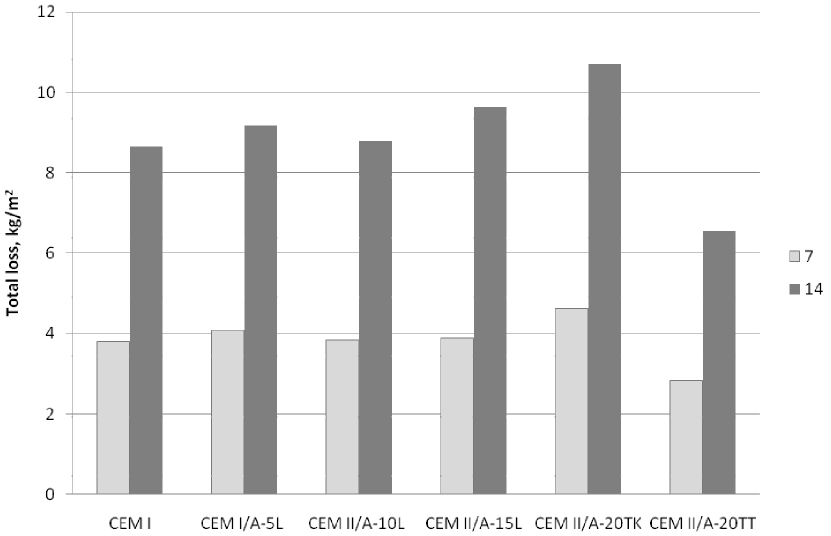

Fig. 2. Total loss of the scaled material from the surface of concrete after 7 and 14 freeze-thaw cycles in 3% NaCl solution. Concretes made with Portland cement (320 kg/m^3) using limestone as a coarse aggregate.

pulverized limestone is obviously greater compared to that of T_T as the second main constituent.

Frost resistance of concretes made with mostly pozzolanic hydration type of burnt oil shale T_K is lower than that of the hydraulic constituent T_T. The second main constituent T_T used in same proportions (20%) causes substantially lower material loss (Fig. 3).

Figure 3 shows the decrease of the frost resistance of concretes made with 15–25% T_K as pozzolanic second main constituent compared to Portland cements made with 0–5% of limestone and 18% of hydraulic constituent T_T. The T_K content higher than 15% causes a decrease in the frost resistance of concrete. Concurrently, the hydraulic type of the second main constituent (T_T) has an increasing influence on the frost resistance in contrast to the pozzolanic (T_K) or inert (L) type of constituent.

Alternate immersion–drying tests were carried out to reveal the influence of the second main constituent on mortar strength and total mass after 20 cycles compared to the results of specimens hardened for 28 days.

The initial mass of mortar specimens was determined after 28 days of hardening. Specimens were weighed after every 48-hour immersion cycle in the water and drying at 100 °C. Fig. 4 illustrates the changes in immersed water content after 20 alternate immersion-drying cycles, depending on the Portland cement type. The test results confirm that increasing the limestone content 5–20% the water immersion of the concrete increases.

Results in Fig. 4 also confirm our assumptions about increasing the water immersion of the pozzolanic type of the second main constituent T_K compared to mostly hydraulic type of the second main constituent T_T.

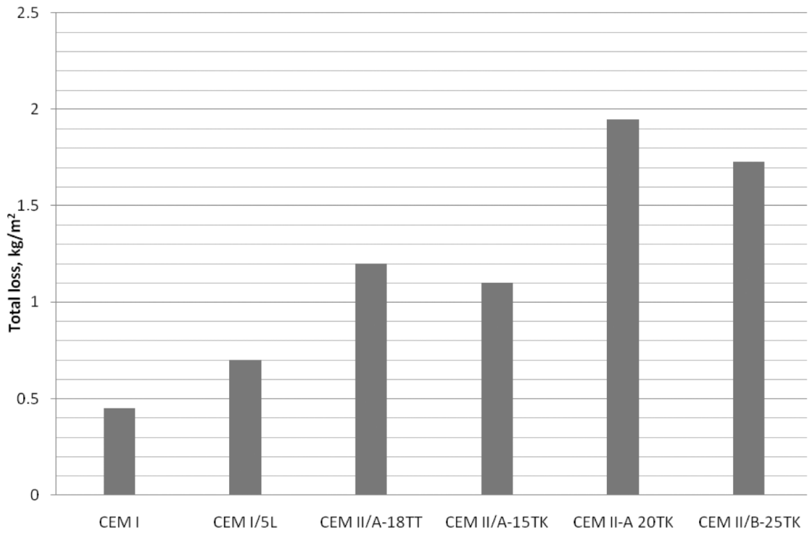

Fig. 3. Total loss of the scaled material from the surface of concrete after 56 freeze-thaw cycles in distilled water. Concretes made with Portland cement (320 kg/m^3) using limestone as a coarse aggregate.

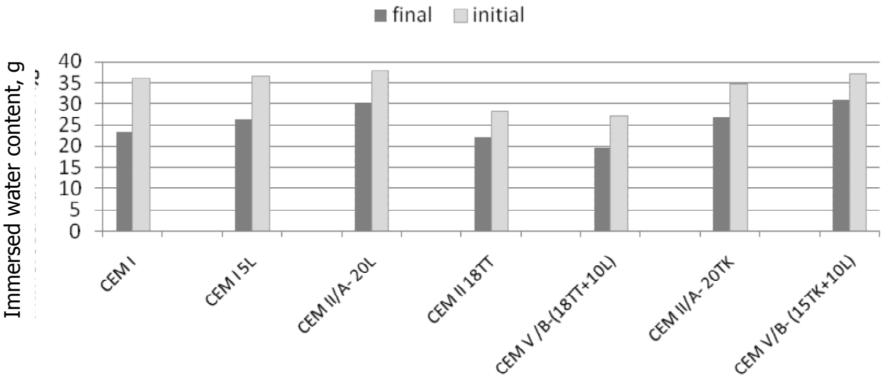

Fig. 4. Changes in immersed water content after 28 days of hardening (initial) and 20 alternate immersion-drying cycles (final).

The highest final water absorption of a specimen occurred in case of cements with 20% limestone content.

Water absorption increases by adding 10% of limestone to the composite cement with 15% T_K (CEM V/B-(15T_K+10L). 10% of the added limestone causes small extra water absorption compared to CEM II/A-20T_K. Compressive strength of specimens made with 5 and 20% of limestone has also decreasing tendency after alternate immersion-drying. The compressive strength of the Portland cement made with 20% of limestone decreased 4% after 20 cycles of alternate immersion-drying compared to the compressive strength after 28 days of hardening (Fig. 5).

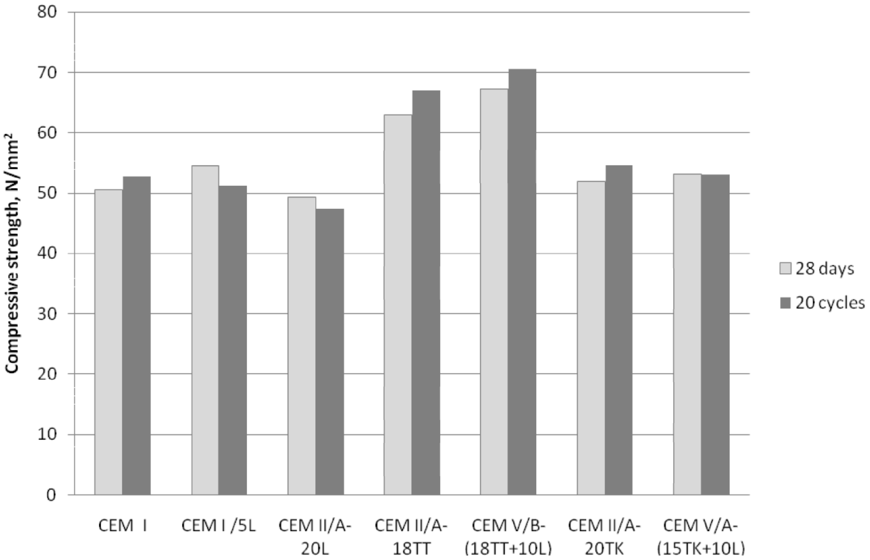

Fig. 5. Compressive strength after 28 days of hardening and 20 alternate of immersion-drying cycles.

The compressive strength of the Portland cement CEM I without any other main constituents increased 6% after 20 cycles of alternate immersion-drying compared to the initial compressive strength after 28 days of hardening. CEM I specimens had no obvious signs of destruction. After 20 cycles the test specimens made with 20% of limestone had obvious signs of deterioration. Specimens with 5%L content had no visible signs of deterioration, despite of decrease in their compressive strength.

Conclusions

Increase in compressive strength of the concrete exposed to alternate wetting-drying indicates continuous hydraulic or pozzolanic reaction in the cement stone. Extra amounts of hydration products induce decrease in the final water absorption compared to the initial characteristics and an increase in the compressive strength and the freezing resistance of concrete.

Sensitivity of the concrete to alternate wetting-drying is revealed in increased water adsorption and decreasing compressive strength. Mainly pozzolanic T_K is more sensitive to alternate wetting–drying and leads to lower frost resistance compared to the mainly hydraulic T_T.

Frost resistance of concretes made with mostly pozzolanic hydration type of burnt oil shale T_K is decreased compared to the hydraulic constituent T_T.

Limestone as an inert second main constituent (with content higher than 5%), causes a decrease in frost resistance and an increased sensitivity to alternate wetting-drying compared to the Portland cement CEM I concrete.

Exposed to alternate immersion-drying conditions, concretes made with the pozzolanic low temperature burnt oil shale T_K show higher water absorption and lower compressive strength than concretes made with the hydraulic high temperature burnt oil shale T_T.

REFERENCES

1. *Hooton, R. D., Thomas, M. D. A.* The Use of Limestone in Portland Cements: Effect on Thaumasite Form of Sulfate Attack // Portland Cement Association R&D 2002. Serial No. 2658. P. 1–9.
2. *Lee, S. T., Hooton, R. D., Jung, H. S., Park, D. H., Choi, C. S.* Effect of limestone filler on the deterioration of mortars and pastes exposed to sulfate solutions at ambient temperature // Cement Concrete Res. 2008. Vol. 38, No. 1. P. 68–76.
3. *Tosun, K., Felekoglu, B., Baradan, B., Altun, A.* Effects of limestone replacement ratio on the sulfate resistance of Portland limestone cement mortars exposed to extraordinary high sulfate concentrations // Constr. Build. Mater. 2009. Vol. 23, No. 7. P. 2534–2544.
4. *Tsivilis, S., Batis, G., Chaniotakis, E., Grigoriadis, G., Theodossis, D.* Properties and behavior of limestone cement concrete and mortar // Cement Concrete Res. 2000. Vol. 30, No. 10. P. 1679–1683.
5. *Tsivilis, S., Tsantilas, J., Kakali, G., Chaniotakis, E., Sakellariou, A.* The permeability of Portland limestone cement concrete // Cement Concrete Res. 2003. Vol. 33, No. 9. P. 1465–1471.
6. *Voglis, N., Kakali, G., Chaniotakis, E., Tsivilis, S.* Portland-limestone cements. Their properties and hydration compared to those of other composite cements // Cement Concrete Comp. 2005. Vol. 27, No. 2. P. 191–196.
7. *Matschei, T., Lothenbach, B., Glasser, F. P.* The role of calcium carbonate in cement hydration // Cement Concrete Res. 2007. Vol. 37, No. 4. P. 551–558.
8. *Raado, L., Nurm, V.* Properties of fluidized bed burnt oil shale ashes // ESCS European Symposium on Service Life and Serviceability of Concrete Structures / A. Sarja (Ed.). Espoo: Concrete Association of Finland, 2006. P. 200–205.
9. *Raado, L., Nurm, V.* Burnt oil shale – main constituent of Portland cement // CESB Proceedings / V. Sruma, Z. Srumova (Eds.). Prague: Czech Sustainable Building Society, 2007. Vol. 2. P. 746–751.
10. *Kikas, V., Ojaste, K., Raado, L.* Ursache und Wirkungsweise der Alkalireaktion in den aus estnischem Portlandölschieferzement hergestellten Betonen // ZKG Int. 1999. Vol. 52, No. 2. P. 106–111.

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