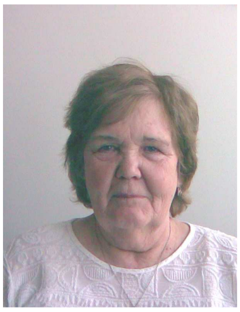
BURNT OIL SHALE – MAIN CONSTITUENT OF PORTLAND CEMENT

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Summary

Oil shale is a major natural resource of Estonia. The power plants use oil shale as a fuel despite its very low calorific value of 8-14 MJ/kg. Oil shale consists approximately of 55-65 % of inorganic matter. Since 1960, the finest fraction burnt at >1300 ^oC and collected by electric precipitators has been used as the main constituent of CEM II. Today in the renovation process, the high temperature system of boilers is being replaced with fluidized bed firing at 800 ^oC.

High temperature burnt oil shale (PP) is the only main constituent of Portland cement that reduces the water requirement of cement.

Low temperature oil shale fly ash (F) particles have different shape and surface.

Keywords: Burnt oil shale, combustion temperature, durability, concrete, Portland burnt oil shale cement

1 Introduction

Burnt oil shale has been used as the main constituent of Portland cement to enhance the quality of Portland cement, at the same time economizing natural resources and using wastes of power plants.

Portland cement with the second main constituent has specific properties. Differences in the properties are in direct dependence of the type and content of the second main constituent.

Fly ash as the by-product of the power plants has wide scale variations in its properties. The type of combustion and dust collection equipment has direct impact on the mineralogical composition, structure and shape of fly ash particles [1]. As a result, Portland cement is provided specific properties, the characteristics of the main constituent used.

The second main constituent of Portland cement, in contrast to clinker, does not have such a high content of CaO saturated minerals as alite $3CaO \times SiO_2$, tricalcium aluminate $3CaO \times Al_2O_3$ and celite $4CaO \times Al_2O_3 \times Fe_2O_3$. Consequently, Portland cement with the second main constituent has a lower content of these minerals. The increasing content of the second main constituent has a decreasing influence on the content of the clinker minerals.

Most of these materials have large specific surface and an increasing impact on cement water demand, respectively. All the types of Portland cement specified in EN 197-1 have a higher water demand than the corresponding Portland cement. Regarding fly ashes, EN 197-1 sets limitations to the CaO_{free} content, to avoid soundness problems. Late hydration of the dead burnt CaO_{free} is the main reason for extra expansion of cement stone as well as concrete cracking.

An inorganic material content of oil shale is about 55-65 % by mass. The chemical composition of the burnt oil shale obtained by electrostatic precipitators is not directly related to the boiler type and combustion temperature. At the same time, differences in the mineralogical composition and distribution of particle size are directly dependent on the abovementioned considerations. This means also that they have a direct influence on the hydraulic properties of fly ash.

2 Chemical and mineralogical composition of burnt oil shale

High temperature burnt oil shale collected by electrostatic precipitators of pulverized fuel combustion boilers (PP) used to produce Portland cements type CEM II/A-T; CEM II/B-T, and composite cements CEM II/A-M; CEM II/B-M(T-L) must have characteristic values set in the requirements of the standard EVS 636:2002.

Estonian standard EVS 636:2002 defines burnt oil shale for the production of Portland cement as the material consisting of the clinker phase mainly of dicalcium silicate, monocalcium aluminate; glassy phase with latent binding properties and pozzolanic SiO_2. The other components are calcium sulphate and fine particles of CaO_{free}. Common constituents of PP are CaO, SiO_2, Fe_2O_3, Al_2O_3, MgO, Na_2O, K_2O, Cl^- and SO_3.

Tab. 1 shows the comparative values of characteristic properties from various standards. Variations in these values cause changes in the characteristic properties of the produced Portland cements. The amount of different burnt oil shale constituents used in Portland cement depends on the acceptance of the requirements EVS-EN 197-1:2002.

The material used as the fuel, boiler type, combustion temperature, and the type of the dust collector system have a conclusive impact on the chemical and mineralogical composition of burnt oil shale ash.

Tab. 1 Comparative requirements for various types of burnt oil shale and fly ash

Symbol	Burnt oil shale (PP) >1300 °C EVS 636: 2002	Burnt shale (T) EN 197-1.2002	Fly ash (V,W) EN 197-1.2002	Fly ash for concrete EVS-EN 450-1:2005
β-$2CaOxSiO_2$	+	+	+	
$CaOxAl_2O_3$	+	+	+	
Reactive CaO,%	+	+	for (V)<10 and (W)>10-15	≤10
CaO_{free},%	≤12.5		for(V) ≤1	≤2.5
Reactive SiO_2 %	+	+	for(V) ≥25 for(W)≥25	≥25

Reactive Al_2O_3%			+	+
SO_3%				≤3.0 %
LOI, % mass		<5	<5, <7	<5; <7; <9
Cl^-,%	≤0.42			≤0.1
Na_2O, %				≤5.0
MgO,%				≤4.0
Specific surface,m^2/kg	≥320			
Hydraulic properties -(by EN196-1): 28 d compressive strength -pozzolanic -hydraulic	≥25 N/mm^2 + +	≥25 N/mm^2 + +	For calcareous ≥10 N/mm^2 + -(+)	28d ≥ 75 % and 90d ≥ 85 % from same for PC
Soundness (EN196-3):	≤10mm	≤10mm	≤10mm	≤10mm
Medium particle size	4μm		On 40μm 10-30 %	Total residue on 0.045 mm
Temperature of combustion	1300- 1400 ^oC	800 ^oC		

Tab. 2 gives the results of the chemical and mineralogical compositions of two different types of burnt oil shale from electrostatic precipitators of high temperature (>1300 ^oC) pulverized fuel traditionally used in Estonia (burnt oil shale PP) and low temperature (800 ^oC) fluidized bed (burnt oil shale F) boilers.

Tab. 2 Mineralogical and chemical composition of burnt oil shale for Portland cement production PP (high temperature >1300 ^oC pulverized fuel combustion boiler) and burnt oil shale F from fluidized bed boiler (low combustion temperature, 800 ^oC)

Property	**Composition, % by mass**	
	PP	$F_{average}$/ $F_{1,}$ F_2,$F_{3,}$$F_4$
$2CaOxSiO_2$	11.0	5.6
$CaOxAl_2O_3$	1.3	0.6
CaO_{free}	9.1	6.1
$CaCO_3$	5.3	13.0
$CaSO_4$	12.2	9.3
K_2O	5.2	4.6
Na_2O	0.2	0.2
SO_3	7.2	/4.8; 4.9; 4.9; 7.2
Cl^-	0.4	/0.3; 0.4 ;0.5 ;0.9
Glassy phase content:		
SiO_2	12.8	8.8
Fe_2O_3	3.6	3.3
Al_2O_3	7.9	5.62
CaO	7.3	/3.7-9.7
MgO	3.0	2.9
Glassy phase sum	34.6	/24.6-31.5
Insoluble in 3% HCl residue, IR	21.7	/35.4-27.6
LOI	2.34	5.7
Reaction ability, CaO mg/g	14.9	/19.2; 25.1; 46.7; 91.7

Tab. 2 shows that no conclusive differences exist in the chemical composition of PP and F. The content of Cl^-, SO_3, CaO, glassy phase, insoluble residue and reaction ability of F from various fields of electrostatic precipitators are different.

Obvious differences exist in the mineralogical composition of both types:

- The content of Cl^- and SO_3 is lower in F from the first and the second field. Chloride and SO_3 content for III and IV fields are almost the same with the content of PP
- Average reaction ability of PP by binding CaO is 14.9 mg/g. The same from F varies from 19.2 (F_1) up to 91.7 for the fourth field, but the amount of ash caught in the third and the fourth field is very small, less than 10 %
- Average insoluble residue content and loss of ignition are higher for F
- The most remarkable differences exist in the content of Portland cement clinker minerals, glassy phase and decomposed $CaCO_3$. The content of clinker minerals and glassy phase of F is lower and the content of decomposed $CaCO_3$ is higher.

The mineralogical composition of burnt oil shale depends directly on the combustion temperature.

Differences in the mineralogical composition predict differences in the binding properites of both Portland burnt oil shale cements, accordingly.

3 Structure and physical properties of various burnt oil shales

High temperature burnt oil shale PP has spherical particles covered with smooth glassy material. PP with particle size ≤10 μm (Fig.1A). Common specific surface of PP used for Portland cement production is about 400 m^2/kg.

Low temperature burnt oil shale F has an indefinite geometric configuration Figure 1B shows F particles with porous stratified surface. Tested specific surface by Blaine is 584 m^2/kg. Figure 1C shows the shape of ground F particles with specific suface 1040 m^2/kg.

Burnt at ≥1300 °C oil shale ash (PP) | Burnt at ≥800 °C oil shale ash (F) | Burnt at ≥800 °C oil shale ground ash (F_g)

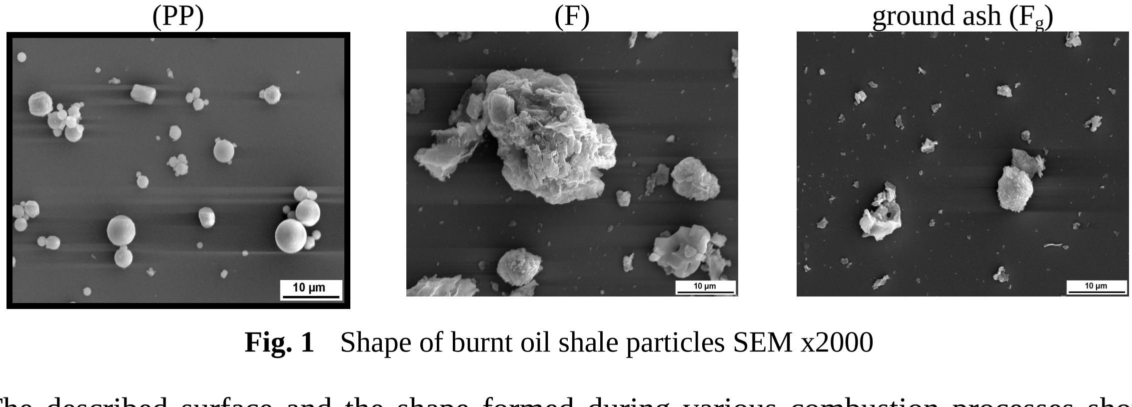

Fig. 1 Shape of burnt oil shale particles SEM x2000

The described surface and the shape formed during various combustion processes show changes in the binding properties of burnt oil shale from hydraulic to pozzolanic.

Using low temperature burnt oil shale F as the main constituent of Portland cement, these changes lead to an increasing water demand. **Tab. 3** gives workability results of the tested Portland cements with 20 %F and PP. The results indicate that water demand of F is higher than that of the other types.

4 Strength properties of various burnt oil shales

Variations in the mineralogical composition, high content of decomposed $CaCO_3$, particle shape and surface formation in the combustion process have direct impact on the hydraulic properties of burnt oil shale as the main constituent of Portland cement.

Tab. 3 Workability of Portland cement mortar 1:3 with W/C = 0.5 made by EN 196-1

	Portland cement	**Portland cement with 20 % PP**	**Portland cement with 20 % F**
Workability of standard mortar G, mm	153	185	145

Test results of **Tab. 4** show a decrease in the hydraulic properties and increase in the water demand of low temperature burnt oil shale F.

Tab. 4 Results of hydraulic properties of various burnt oil shale mortars (1:3 = burnt shale: sand) tested by EN 196

Type of burnt oil shale	**W/C**	**G,mm**	**Compressive strength 28 d, N/mm^2**
F1	0.9	201	3.9
F2	0.89	199	4.8
F3	0.83	179	6.8
F4	0.83	188	7.1
PP	0.41	195	11.7

5 Characteristic properties of Portland oil shale cements and Portland cement

Results of **Tab. 5** show alterations in the compressive strength and soundness of mortar prisms 4×4×16 cm made with various types and content of burnt oil shale (PP and F) and 10 % pulverized limestone (L). Portland cement and Portland limestone cement with 10 % limestone were used as reference cements. Prisms were made with the same water-cement ratio, W/C = 0.5.

Test results show a slight decrease of the early strength for Portland cements made with low temperature burnt oil shale F as compared to the same for Portland cement and Portland limestone cement mortar:

- An increase of the F content causes a decrease of the early strength. The early strength of Portland cement with an inert constituent, ground limestone, has a significant decrease.
- The content of low temperature burnt oil shale of Portland cement has no direct impact on the standard strength (28 days).
- 20 % content of high temperature burnt oil shale PP has a decreasing impact on the compressive strength caused by the amount of mixing water content, too high for this cement amount of (equal to W/C ratio 0.5 of other types). The workability of Portland burnt oil shale (20 %PP) is G = 185 mm. The same for the Portland cement mortar is 157 mm and for Portland cement with 20 %F is 145 mm, accordingly.

Soundness tests results show no direct impact of low temperature burnt oil shale, in contrast to Portland cement. Expansion shows a slight decreasing effect with an increase of the F content.

Portland cements with the PP content have higher expansion caused by CaO_{free}. The values comply with the EN 197 requirements.

Tab. 5 Results of compressive strength and soundness tests with various types of Portland cement

Type of Portland cement	**G, mm**	**Compressive strength, N/mm^2 of standard mortar prisms 4x4x16cm made by method EN 196**					**Soundness, mm Le Chatelier**
		2	7	28	56	91	
Portland cement	157	32.8	49.3	58.3	63.2	63.5	1.0
Portland cement with 10%F	156	31.3	49.0	57.6	61	63.0	1.5
Portland cement with 20%F	145	31.4	46.6	55.8	61.5	63.7	1.0
Portland cement with 10% L	160	31.5	44.2	52.3	55.9	58.1	0.5
Portland cement with 20% PP	185	29.3	39.6	49.9	56.4	62.9	4.9

Thus, the lower content of CaO_{free} and large specific surface of the low temperature material F have a decreasing impact on the expansion value.

Test results of 24-hour hydration heat carried out by the Laboratory of Kunda Nordic Cement Plant show a 10 % decrease in the hydration heat of Portland cement made with a 20 % F content, in contrast to Portland and Portland burnt oil shale cement made with a 20 %PP.

6 Conclusions

Low temperature combustion of low calorific fossile fuel oil shale causes changes in the mineralogical composition and in the structure of particles caught by electrostatic precipitators. This results in the developement of pozzolanic properties in low temperature burnt oil shale F, in contrast to hydraulic properties in high temperature burnt oil shale PP. Changing properties cause alterations in the characteristic properties of Portland burnt shale cement produced with low temperature burnt shale F.

SEM analyses of combustion products were made by The Centre for Materials Research of TUT

References

[1] RAADO, L.M, NURM,V. *Properties of fluidized bed burnt oil shale ashes.* Proc. of European Symposium on Service Life and Serviceability of Concrete Structures ESCS-2006, Finland, pp.200-205

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