Comparison of Clinkers Produced Using Different Layers of Oil Shale

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INTRODUCTION

Oil shale is one of the largest energy resources today. Oil shales are horizontally layered rocks that have rich organic content called kerogen and mineral part is usually composed of clay, quartz, and carbonates such as calcite and dolomite [1]. Oil shale can be used either to extract liquid hydrocarbons or to burn directly to produce electric energy. Due to their different origins, oil shales have different calorific values because of the variation in the content and composition of kerogen. The composition of the mineral matrix in oil shales also varies. Oil shales can be classified into three categories based on mineral composition: carbonate-rich shale, siliceous shale and cannel shale [2]. Silica-rich oil shale ashes are likely to develop pozzolanic properties whereas carbonate-rich materials can also develop hydraulic properties. Oil shale has been used for cement production in Estonia, Germany, Russia, China, and the USA.

The inorganic part of oil shale can be an attractive source of raw materials for the cement industry. Oil shale can replace the typical raw materials in clinker, such as clay, without significantly changing the mineral composition of clinker, which is especially valuable for the Israeli cement industry. Israel has proven reserves of oil shale that are currently not developed in sufficient volume [3]. Earlier, the experimental power plant, which produced electric energy by burning oil shale, operated by the PAMA Company that began operation in 1989 and has since been closed, because the grade of the Rotem oil shale was not uniform (the calorific value ranged from 2.7 to 5 MJ/kg). In addition, Israeli oil shale has a high ash content, which also negatively affects its use as a fuel in power plants. Also, the calcium oxide contained in the ashes is active and reacts with carbon dioxide to form calcite. Calcite, in turn, reacts with sulfur dioxide and forms anhydrite, which deposits hard plaque on the surface of equipment reducing the efficiency of thermal power plants [4]. In combination with low organic content, the use of oil shale for the production of electricity becomes ineffective from an economic and practical point of view.

Previous research demonstrated that oil shales ashes from Israeli power plant Pama contain clinker minerals, anhydrite, calcite, free lime, quartz, and potentially could be used as a binder [5]. Based on this preliminary conclusion, oil shale can be used as a substitute material for clinker production for Portland cement is feasible. Portland cement is made primarily from finely ground clinker, which itself is composed of calcium silicate and aluminate minerals formed when limestone and clay are burnt at high temperatures. Limestone serves as a source of calcium, and clay serves as a source of silica, alumina, and iron. These minerals are generally mined in open quarries. Israel has sufficient resources of limestone to supply the needs of the cement industry for the next 20 years, but the clay is already in short supply. Oil shale can be used as fuel and raw material in clinker kilns, as cement clinker manufacture requires energy and minerals. The usage of oil shale can significantly reduce fuel consumption in a rotary kiln, which can be beneficial for the environmental situation due to the reduction of CO_2 emissions to the atmosphere.

The primary aim of this study is to research the potential of Israeli oil shale utilization as a raw clinker material for production clinker for Portland Cement. In this research, the oil shales from Northern Negev, Israel were used. The oil shales of 2 types were studied: upper layer (poor in organic part), the lower layer (rich in organic part) according to the occurrence in oil shale deposition. Many technological aspects, as well as properties of the produced cement, depending on the properties of local oil shale. For this reason, the objective of the current research is the study the physical properties, chemical and mineral composition of raw Israeli oil shale as a potential material for cement production. Another part of the study is the calculation of the clinker raw meal composition for upper and lower oil shale layers, determination of the energy released during the burning process and the mineral composition of the produced clinker.

RESULTS

The oil shales from Ghareb Formation mined from quarry Mishor Rotem, Northern Negev, Israel were investigated. Mineral and chemical composition of oil shale were determined using x-ray diffraction (XRD) and inductively-coupled plasma (ICP) spectroscopy, respectively. The results are presented in Table 1. It can be concluded from Table 1 that Israeli oil shale belongs to the carbonate-rich oil shales. Silica content in oil shale was low. Therefore its ashes will not be pozzolanically active. However, chemical composition shows, in addition to calcium oxide, the presence of three other main oxides required for clinker: silica, alumina and iron oxide.

Table 1. Mineral and chemical composition of upper and lower raw oil shale layers, % wt.

	Upper layer	**Lower layer**
Calcite	62.2	59.8
Quartz low	2	2.2
Apatite	0.6	1.8
Anhydrite	0.4	0.4
Gypsum	8.4	15.7
Potassium Phosphate	0.6	1.5
Pyrite	0.9	2.2
Amorphous	24.8	16.3

	Upper layer	**Lower layer**
CaO	35.6	37.5
SiO_2	10.5	9
Al_2O_3	4.4	3.3
Fe_2O_3	2	1.9
MgO	0.5	0.6
TiO_2	0.19	0.14
K_2O	0.32	0.38
Na_2O	0.19	0.15
P_2O_5	1.02	2.61
Mn_2O_3	0.01	0
SO_3	3.7	4.6
LOI	38.3	40.4

The presence of phosphorus can have a significant impact on the clinker quality and production process. Therefore, the use of oil shale as a raw material for clinker can be limited by the concentration of phosphates in it. Calorific values as determined by DSC were 1.97 MJ/kg and 3.616 MJ/kg for upper and lower oil shale layers, respectively.

The target chemical composition of the clinker and chemical composition of each layer of oil shale after burning are presented in Table 3. Based on target mineral composition and clinker moduli (LSF– lime saturation factor, SR–silica ratio, AR–alumina ratio), the maximum oil shale content in the raw meal was calculated as 35 and 39% for upper and lower layer, respectively.

The results of the thermal analysis of raw meals are presented in Figure 2. It can be seen that dehydration takes place in the range between 30 and 150 °C. In a temperature range from 200 to 600 °C, the major mass loss is due to the decomposition of organic components of oil shale. In a temperature range from 650 to 900 °C, there is the highest mass loss, which is mainly due to the decomposition of calcium carbonate. Above 1100 °C the formation of clinker minerals takes place. With regards to the energy contribution of oil shales to clinker production, it can supply energy from the burning of the organic fraction at the stages of preheating and calcination. Oil shale can provide 0.7 MJ/kg and 1.4 MJ/kg of clinker for upper and lower layers, respectively.

Table 3. Target clinker composition and moduli for lower and upper layers

	Upper layer	**Lower Layer**	**OPC Clinker**
CaO, %	57.7	62.9	[63 - 67]
SiO_2, %	17.0	15.1	[21 - 24]
Al_2O_3, %	7.1	5.5	[4 - 8]
Fe_2O_3, %	3.2	3.2	[2 - 4]
Energy, MJ/kg	1.97	3.62	[1.68-3.74]

	Upper layer	**Lower layer**	**OPC Clinker**
Content	35%	39%	
LSF	0.93	0.95	[0.92-0.98]
SR	2.34	2.37	[2-3]
AR	1.53	1.86	[1-4]
C_3S	56.5	59.8	[50-70]
C_2S	18.5	15.2	[15-30]
C_3A	8.5	10.1	[5-10]
C_4AF	10.9	9.5	[5-15]

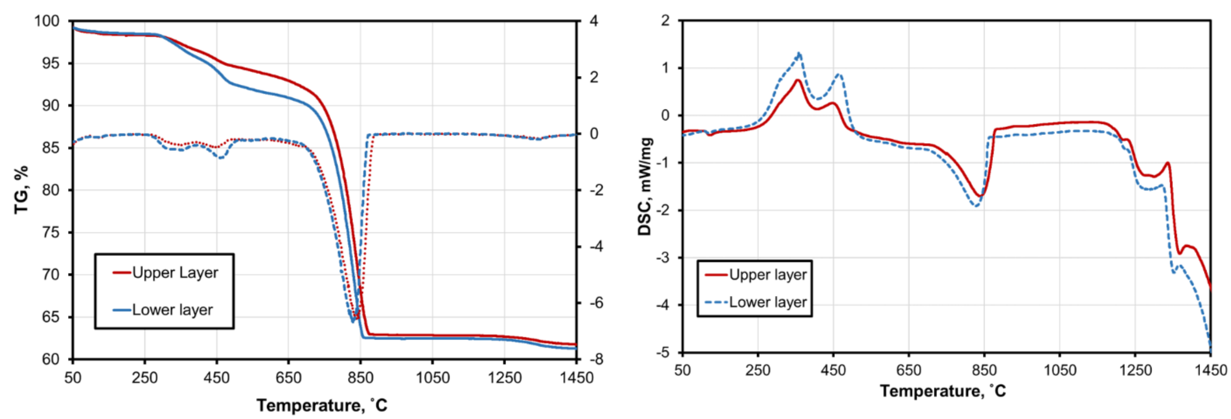

Figure 2. TGA and DTG (left) and DSC (right) curves of raw clinker meals in a dry air atmosphere.

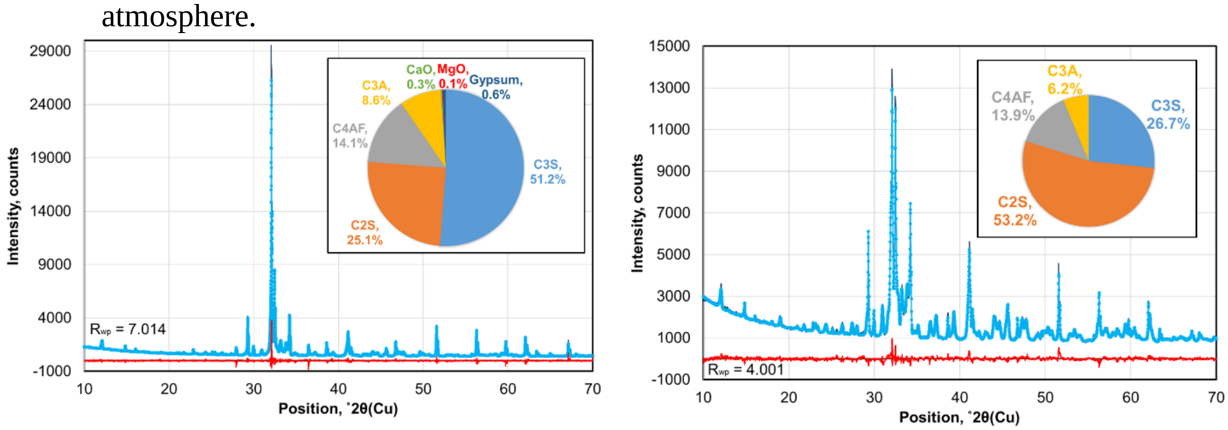

Figure 3. XRD diffractogram and phase composition of clinker with oil shale 35% (Upper layer)

Figure 4. XRD diffractogram and phase composition of clinker with oil shale 39% (Lower layer).

The clinker raw materials and burned oil shale were weighted and mixed with water to form nodules that were dried in an oven. Clinker nodules were burned at 1450 °C and cooled at the rate of 20 °C per minute to produce clinker. XRD diffractogram of the clinker with oil shale from the upper layer and lower layers are presented in Figures 3 and 4. From these diffractograms is clear that the clinker rich in alite was obtained from the upper layer and clinker rich in belite was obtained from the lower layer. This can be explained by the high concentration of phosphorus oxide in the lower layer of oil shale. For solving this problem magnesium oxide was added as a dopping for stabilizing alite. As shown in Figure 5, alite clinker was obtained with the addition of 1% magnesia.

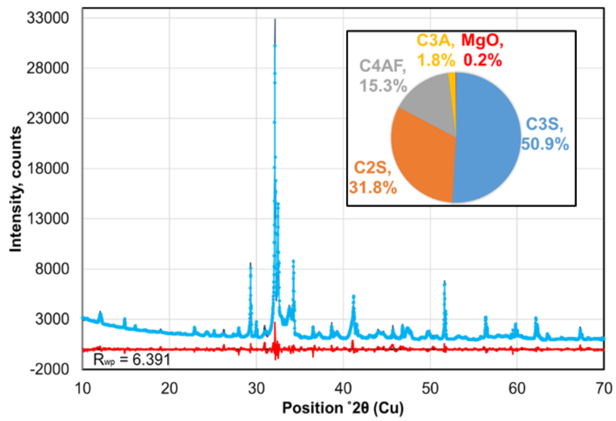

Figure 5. XRD diffractogram of clinker oil shale from the lower layer with the addition of 1% MgO.

CONCLUSIONS

In this study, Israeli oil shale was investigated as a potential raw material for cement production. It was demonstrated that oil shale can replace about 30-40% of raw materials for clinker production. The oil shales can be used unburned partially replacing fuel consumed for clinker preheating and calcination. The lower layer proved the higher potential for clinker production because of lower phosphate content. However, it was demonstrated the problem with phosphates in the upper layer oil shale can be overcome by the use of magnesium dopping.

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