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Utilization of oil shale in the production of Portland clinker

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Abstract

Oil shale can potentially be utilized in manufacturing the Portland cement. In addition to the utilization of the spent oil shale after combustion, it can also reduce the required temperature for the clinkering reactions during the production of Portland clinker. A study on the Jordanian oil shale was performed to maximize the use of oil shale ash in the manufacturing of Portland cement. It was found that Jordanian oil shale can be used up 15% with the typical raw materials to produce Portland clinker without altering its principle properties. The corresponding temperature required to generate the required liquid for the clinkering reactions as well as the essential ingredients for clinker was found to be around 1300 °C. The optimized blend ratio obtained was equal to of 16% oil shale ash, 18% kaolinite, and 66% calcite. The operating temperatures for this optimized blend ratio were found to be between 1300 and 1350 °C. The resulting Portland clinker from this ratio will need further testing in accordance with international standards for Portland cement to examine properties like strength, setting time, etc.

Keywords: Cement; Portland; Oil shale; FACT

1. Introduction

Oil shale is considered one of the largest energy resources in the world. The oil equivalent of oil shale around the world is estimated to be around 30 times the reserve of the crude oil [1]. Jordan is one of the many countries that have large oil shale deposits. These deposits are mainly located in El-Lujjun, Sultani, Jurf Eddarawish, Wadi Mgher, and Khan Ez Zabib. Jordan's limited energy resources have led many investigators trying to utilize the oil shale as a source for liquid fuel.

The high percentage of ash in the Jordanian oil shale (50–60%) makes the future of utilization of oil shale as a source of liquid fuel uncertain. This also led some researchers to study the possibility of using the Jordanian spent oil shale as an additive to the concrete. Smadi and Haddad [2] have reported the possibility of using 10% of spent oil shale produced after retorting process at 600 °C in concrete mixes without significantly affecting its compressive strength. However, the cementing properties of the spent Jordanian oil shale ash are relatively poor. Khedawi et al. [3] performed similar study with emphasis on the Pozzolanic activity of Jordanian oil shale ash. Although, the oil shale ash showed some Pozzolanic activity, it is not as high as the commercial Pozzolanic cement. In different studies for some Israeli oil shales [4,5], it was concluded that the structure and the properties of the spent Israeli oil shale ash is similar to that of ordinary Portland cement.

Although there are number of studies on using spent oil shale ash as an additive or partial replacement to Portland cement in the making of concrete, little information was available on utilizing the oil shale itself in the production of Portland clinker as an energy source for the clinkering process, and as a raw material to make up the cement clinker. Moreover, very few information,

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if any, available on the thermodynamic reactions that occur when utilizing the oil shale in the production of Portland clinker.

In this study, a comprehensive thermodynamic study was conducted to understand the reactions and the phases that exist when utilizing the oil shale in the production of Portland clinker. This study utilizes theoretical thermodynamic equilibrium calculations as well as experimental verifications.

2. Experimental

2.1. Materials

2.1.1. Oil shale

Oil shale standard samples were obtained from El-Lujjun deposits in Jordan. Table 1 presents the main constituents in the oil shale deposit in this study. Laboratory ashes from this oil shale were prepared by initially crushing the oil shale to <150 μm, and ashing in a laboratory furnace in accordance with the Australian Standards [6] for ashing hard coal. A known mass of oil shale is heated in air to 500 °C in 30 min, from 500 to 815 °C in 60 min, and kept at 815 °C for 3 h. The analysis of this oil shale ash is presented in Table 2 as determined using the X-ray fluorescence. The X-ray diffraction was also determined as seen in Fig. 1. The XRD results showed high proportions of free lime (CaO) as well as high amounts of anhydrite ($CaSO_4$). The combination of the XRF and XRD results can provide an approximate analysis of the main minerals present in the ash and this is presented in Table 3. The particle size distribution for oil shale ash is presented in Fig. 2.

2.1.2. Ordinary Portland cement (OPC)

A sample of an OPC was used in this study to try on blending with oil shale ash at different temperatures. The chemical analysis of this sample is presented in Table 4.

Table 1
Analysis of the El-Lujjun deposit

Property	Proportions (wt%)
Hydrogen	2.57
Sulfur	4.54
Organic carbon	17.93
Inorganic carbon	4.87
Moisture	1.11
Volatile matter	43.96
Ash	54.51
Fixed carbon	0.42
Carbonate ($CaCO_3$)	40.58

Table 2
The analysis of the El-Lujjun oil shale ash as determined by the XRF

Component	Proportions (wt%)
SiO_2	26.6
Al_2O_3	7.2
Fe_2O_3	2.9
CaO	43.4
MgO	0.8
Na_2O	0.3
SO_3	9.1
P_2O_5	5.9

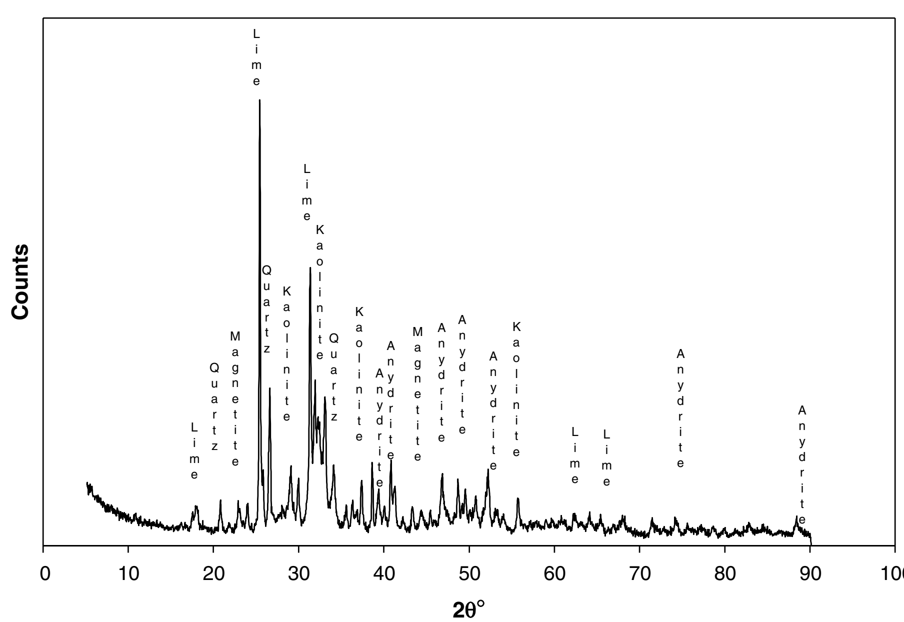

Fig. 1. XRD for the El-Lujjun oil shale ash.

Table 3
The approximate proportions of main minerals in oil shale ash

Mineral	Proportions (wt%)
Anhydrite	15.9
Quartz	23.0
Kaolinite	17.5
Magnetite	3.1
Lime	38.1

2.1.3. Calcite and kaolinite

Samples of naturally occurring calcite and kaolinite were used in the study. The percentage of $CaCO_3$ in the calcite sample was around 97%, with impurities of clays and quartz. Similar purity for the kaolinite with main impurities of calcite, and other clays. Fig. 2 shows the particle size distribution for the calcite and the kaolinite used in this study.

2.2. Thermodynamic calculations

The thermodynamics calculations were performed using FACT; a computer software which is normally used for predictions of multiphase equilibria, liquidus temperatures, and proportions of liquid, and solid phases in certain atmospheres. (For further details see [7].) A comprehensive study for the system Al–Ca–Fe–O–Si for coal ash was presented by Jack [8].

FACT calculations were used in this study to predict the quantities of tricalcium silicate ($3CaO \cdot SiO_2$ or C_3S), calcium orthosilicate ($2CaO \cdot SiO_2$ or C_2S), tricalcium aluminate ($3CaO \cdot Al_2O_3$ or C_3A), and tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ or C_4AF) at different temperatures. These minerals are the most important constituents in any Portland clinker. FACT was also

Table 4
The oxide analysis of Portland clinker used in this study

Component	Proportions (wt%)
SiO_2	23.6
Al_2O_3	5.9
Fe_2O_3	2.3
CaO	65.3
MgO	1.53
Na_2O	0.1
P_2O_5	0.1
K_2O	0.4

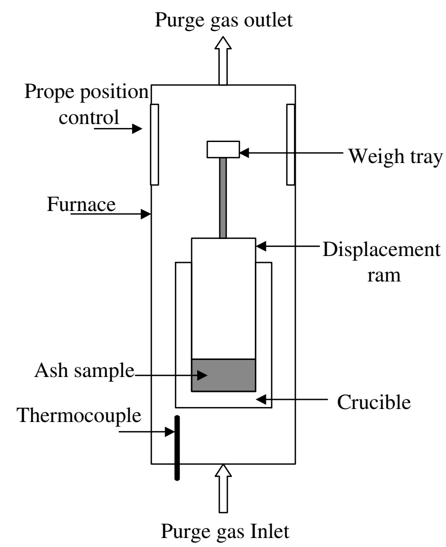

Fig. 3. Schematic diagrams of a thermomechanical analysis (TMA) set-up.

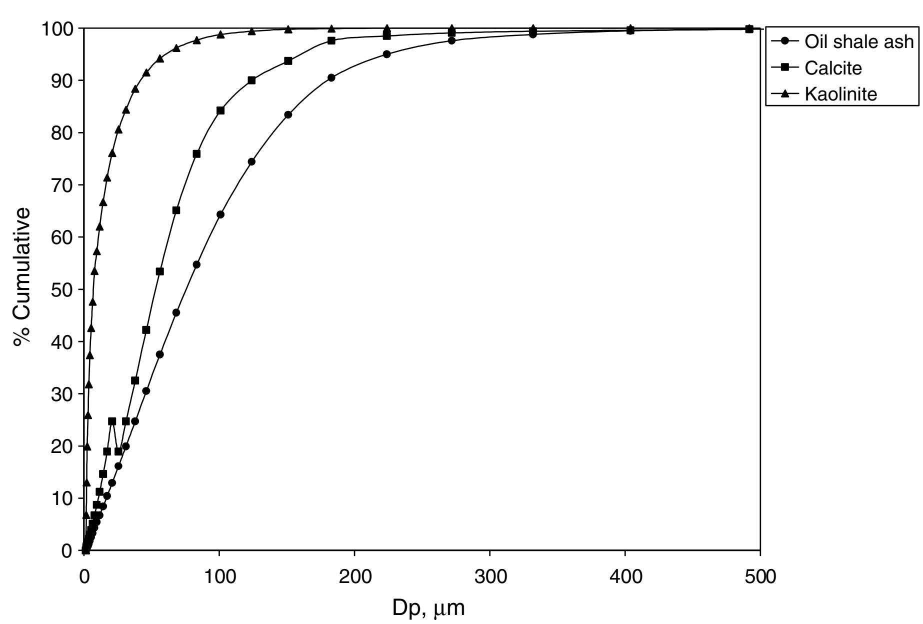

Fig. 2. Particle size distribution for the oil shale ash, calcite, and kaolinite used in this study.

used to estimate the quantities of liquid present at different temperatures.

2.3. Thermomechanical analysis (TMA)

The TMA has previously been shown to determine coal ash fusion characteristics by measuring dimensions of ash pellets heated to different temperatures [9]. In this study, the TMA is used to determine the quantity of the liquid phase present upon heating samples to different temperatures. This also provides verification for the results obtained from the FACT calculations. In this experiment, around 50-mg sample of oil shale ash was initially compressed to 0.35 MPa in a molybdenum

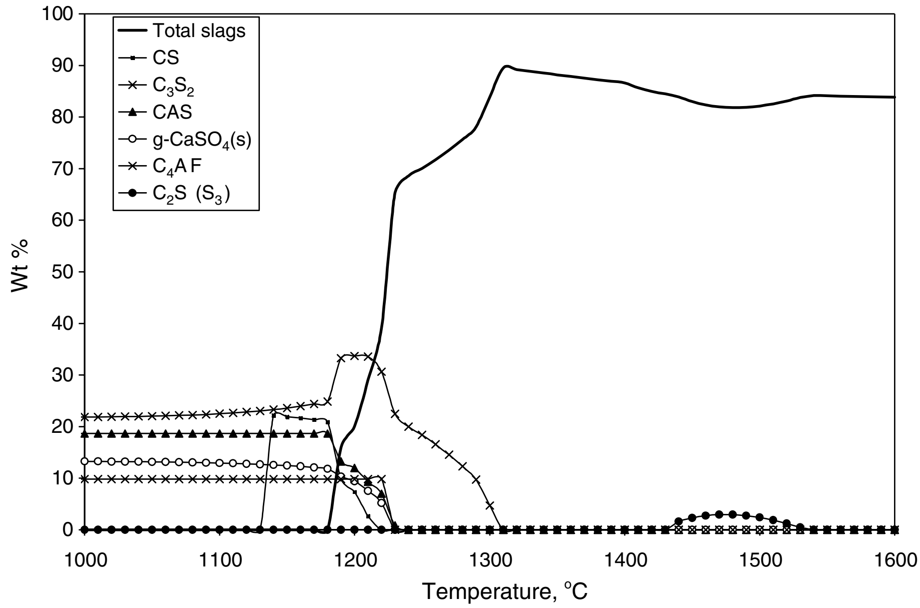

Fig. 4. The thermodynamic equilibrium for the oil shale ash.

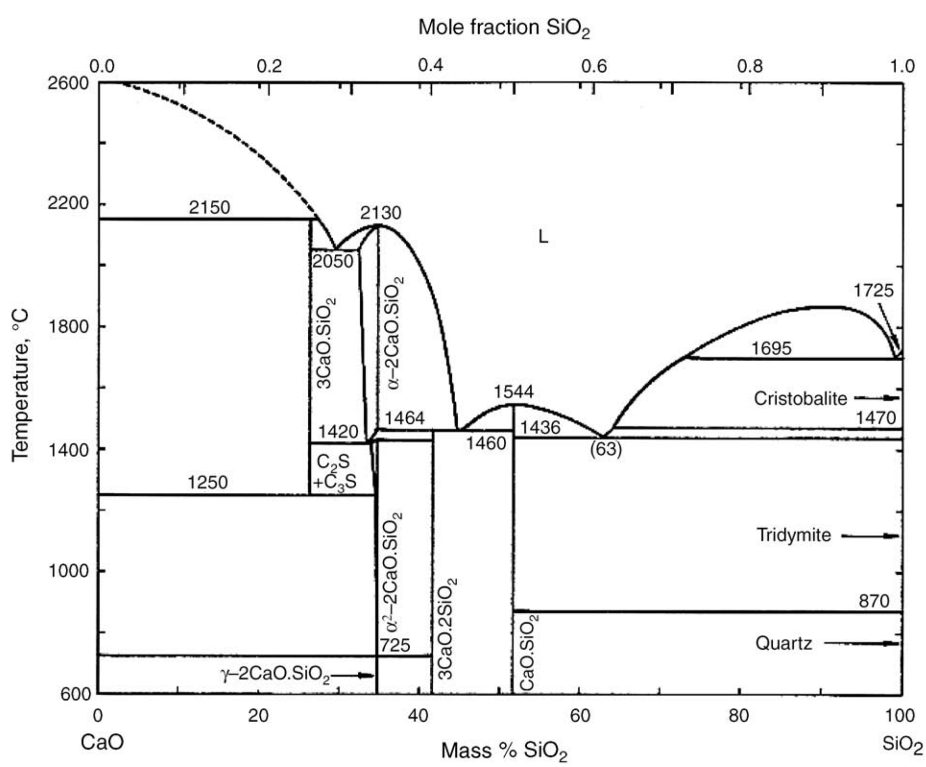

Fig. 5. The phase diagram of the system CaO–SiO_2.

crucible. The molybdenum crucible was placed in the TMA equipment and the system was purged with Argon. The height of the ash pellet was continuously measured while the sample was heated from ambient to 1600 °C at 5 °C/min. TMA experiments were conducted under Argon conditions in order to prevent oxidation of the molybdenum crucible. Fig. 3 shows the crucible set-up in the TMA.

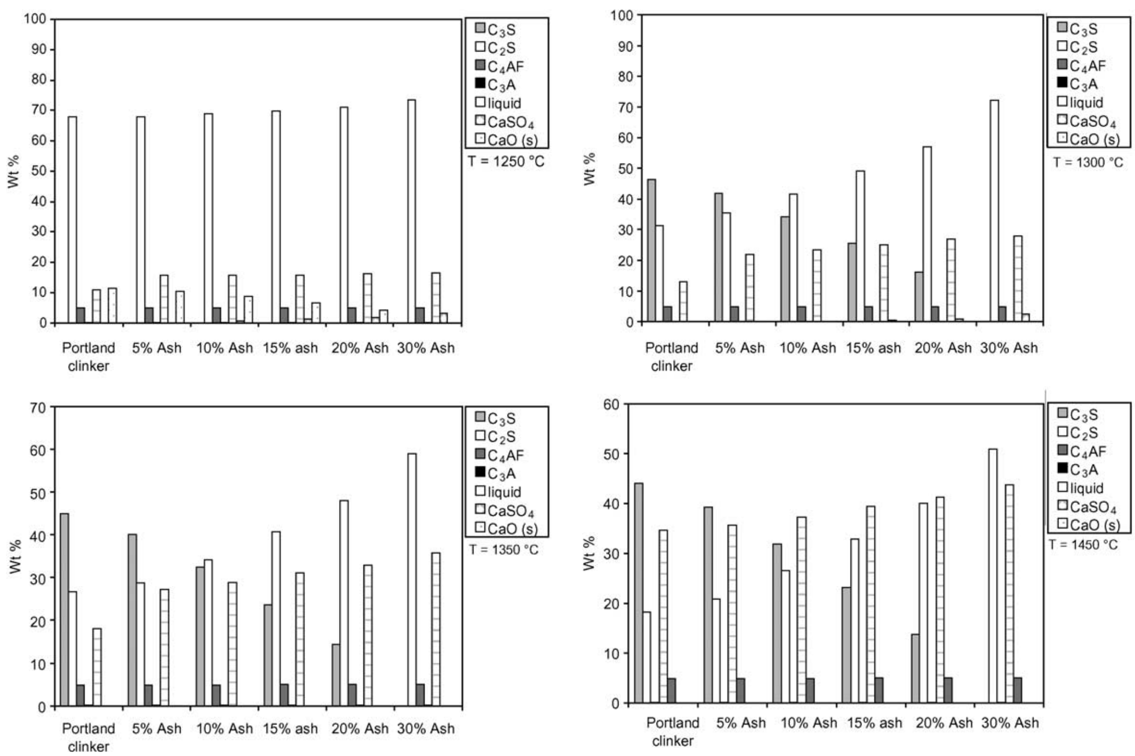

Fig. 6. Main clinker minerals, and liquid phase present after blending oil shale ash with ordinary Portland clinker raw materials at 1250, 1300, and 1350 °C; and 1450 °C, respectively.

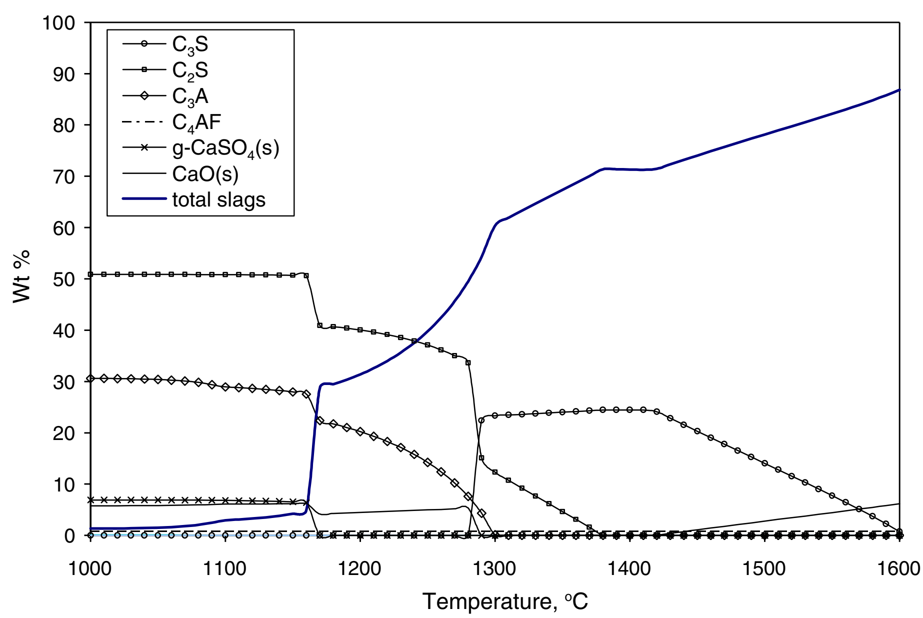

Fig. 7. FACT calculations for the main species present when blending 16% oil shale ash, 18% kaolinite, and 66% calcite.

3. Results and discussion

Fig. 4 presents the results from the thermodynamic calculations for oil shale ash. It is clear that there are large proportions of tricalcium disilicate (C_3S_2), which is not a constituent of Portland clinker, and calcium sulphate present at temperatures up to 1250 °C. A sudden drop of these quantities occurs after 1250 °C, which resulted in formation of liquid glass slag. C_2S only formed below that temperature, with no significant amounts of C_3S, which makes the cementing properties of the oil shale ash very weak. This could be explained by the relatively low quantity of lime present in the ash sample and the large quantity of calcium sulphate that present in the sample. As shown in Fig. 5, the amount of lime to form the C_3S should be from around 65% to 75%. It is worth mentioning that a small amount of α-C_2S starts to precipitate out of the liquid slag above 1450 °C [10].

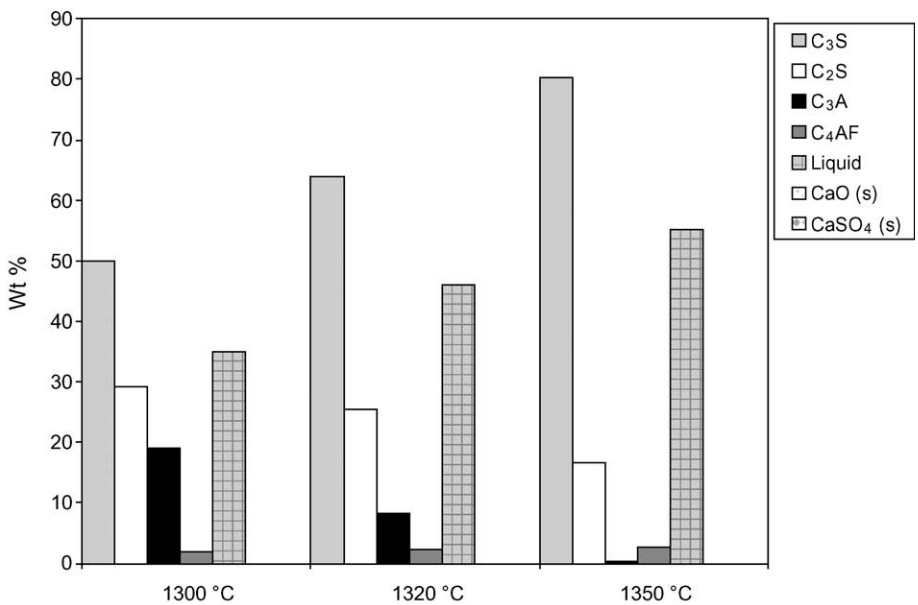

Fig. 8. Summary of the proportion of main clinker components from blending of 16% oil shale ash with 18% kaolinite and 66% calcite.

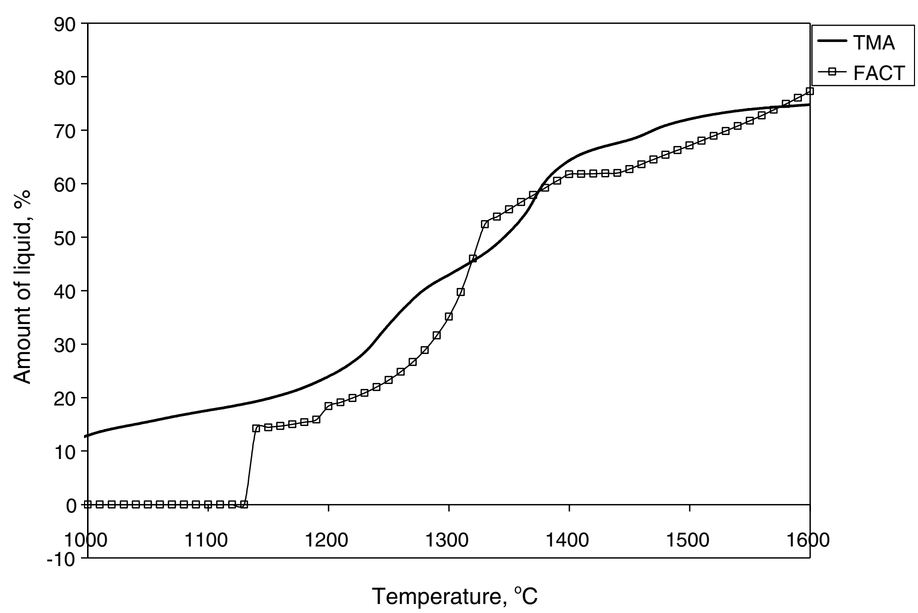

Fig. 9. A comparison between the quantities of liquid phase obtained by FACT calculations, and the TMA trace (Shrinkage). Obtained for the blend of 16% oil shale ash, 18% kaolinite, 66% calcite.

Different blending ratios between oil shale ash and the ordinary Portland clinker raw materials were used in this study in order to determine the possible blending ratio for further processing without affecting the principle properties of ordinary Portland clinker. Fig. 6 presents the minerals that exist, at different temperatures, when blending the oil shale ash with ordinary Portland clinker raw materials. It also presents the amount of liquid glass at every temperature as per calculated in the FACT software. At a temperature of 1250 °C, neither the ordinary Portland clinker nor the ash blends would be a suitable Portland clinker material. This is due to the very low amount of C_3S, which is essential to make up the early strength of concrete. C_3S is reported to be stable in the temperatures between 1300 and 1800 °C [10]. It is also shown in Fig. 5 that at temperatures above 1250 °C and below 1420 °C, the C_2S and C_3S become at equilibrium.

At the temperatures of 1300 and 1350 °C, it is clear that a blend ratio of 10–15% could be used in the making of clinker containing the major two silicate phases. This is due to the formation of relatively higher amounts of C_3S and C_2S, in addition to the C_4AF and C_3A. Unlike the Portland clinker at this temperature, the mentioned blend contains enough liquids to form the clinker during the process of making Portland clinker.

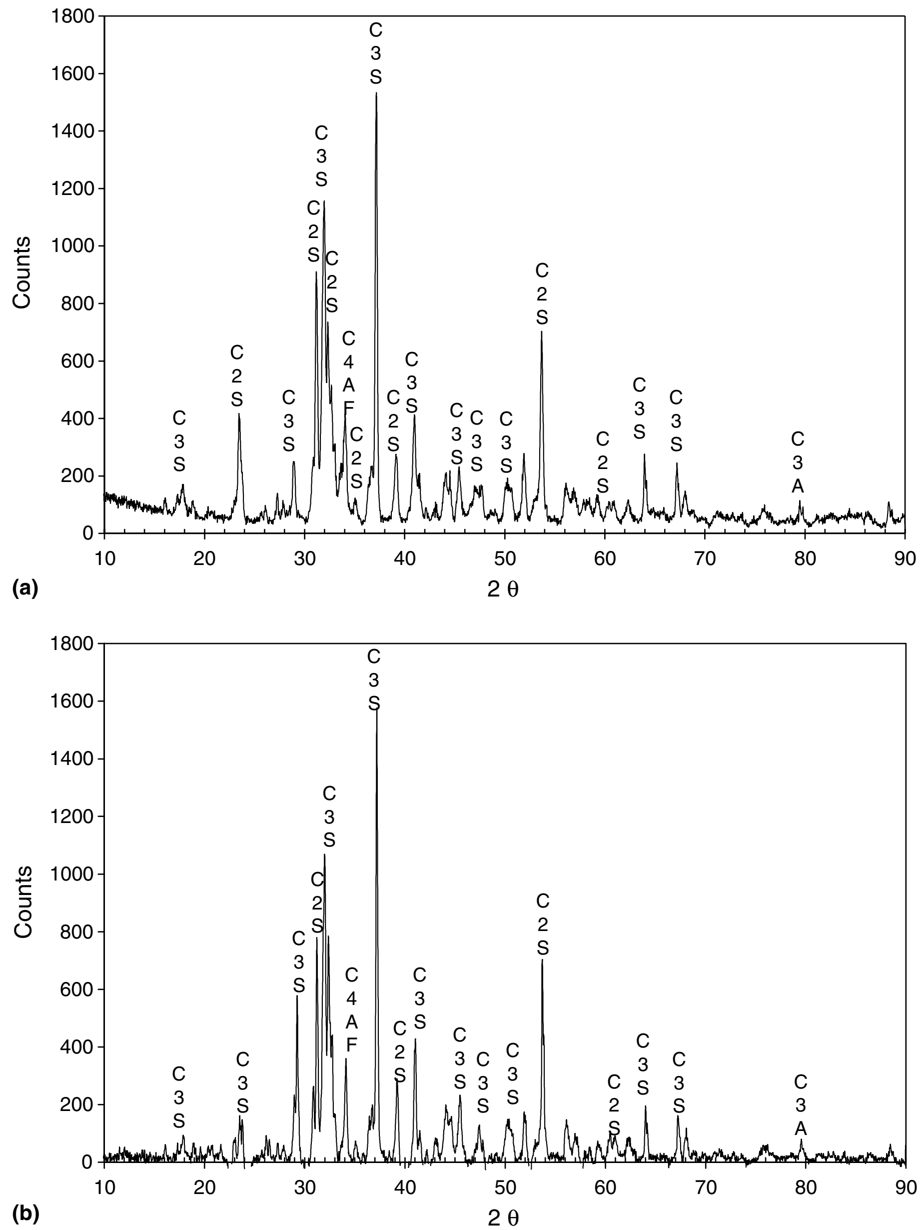

Fig. 10. X-ray diffraction analyses for the suggested blend of oil shale ash, kaolinite, and calcite at (a) 1300 °C and (b) 1350 °C.

It is reported by many researchers that the minimum amount of liquid required for the clinkering reactions is around 20% [10].

For the temperature of 1450 °C, it is clear that a blending ratio up to 15% oil shale ash could be used with the average raw material for the production of Portland clinker. The difference in the ratio of C_3S and C_2S will affect the setting time of the cement as well as its initial strength. However, all the above-mentioned ratios are considered among the standards of ordinary Portland cement.

Different blending ratios of oil shale ash, calcite and kaolinite, which are considered the main raw materials used for the Portland clinker production, were tried using FACT calculations to come up with constituents close to the ordinary Portland clinker. The optimized ratio obtained was 16% of oil shale ash, 18% kaolinite, and 66% of calcite. Fig. 7 presents the main species that present at different temperatures obtained when using the mentioned blend ratio. Significant melting of the constituents occurs after the temperature of 1150 °C, the solid $CaSO_4$ participates in the melting process. As mentioned earlier, the C_3S starts to form above 1300 °C. Further heating would result in lowering the quantity of C_2S which participate in the formation of the liquid phase.

Fig. 8 presents the compound content that exist for the suggested blend ratios at different temperatures. It is clear from that figure that a temperature ranging from 1300 to 1350 °C can be used for that blend ratio to make up all the necessary components of Portland clinker. The variation in temperature would result in a difference in the performance of the resulting clinker. It is important here to mention that at those temperatures the clinker would have enough liquid phase to perform the clinkering reactions.

Further, the thermomechanical analysis (TMA) for the suggested blend ratio was performed in order to verify the amount of liquid phase obtained from FACT calculations. Fig. 9 shows a close profile of the liquid formed at different temperatures, particularly at temperatures higher than 1130 °C. Below this temperature sintering expected to have occurred which results in shrinkage of the pellet. That would result in further reduction in the height of the pellet of the blend. (Further details about the sintering in TMA are given elsewhere [11].) As seen from Table 4, it is important to mention here that the proportions of phosphorous are high in the original oil shale ash. This can be explained by the geological surveys, which have confirmed that major oil shale deposits in Jordan are underlain by phosphate beds. Upon blending with kaolinite and calcite with their proposed proportions.

Samples for the suggested blend at 1300 °C were prepared for the use in the scanning electron microscope. Images for cross sections of the samples were obtained after mounting the treated sample in epoxy resin and polished using alumina grinding wheels. An EDS analyses were also obtained for this blend. It was clear from these analyses that C_3S, and the C_2S are the dominant species present. Fig. 11 presents examples of these phases. Similar results were obtained from the X-ray diffraction analyses at 1300 °C, and 1350 °C as shown in Fig. 10.

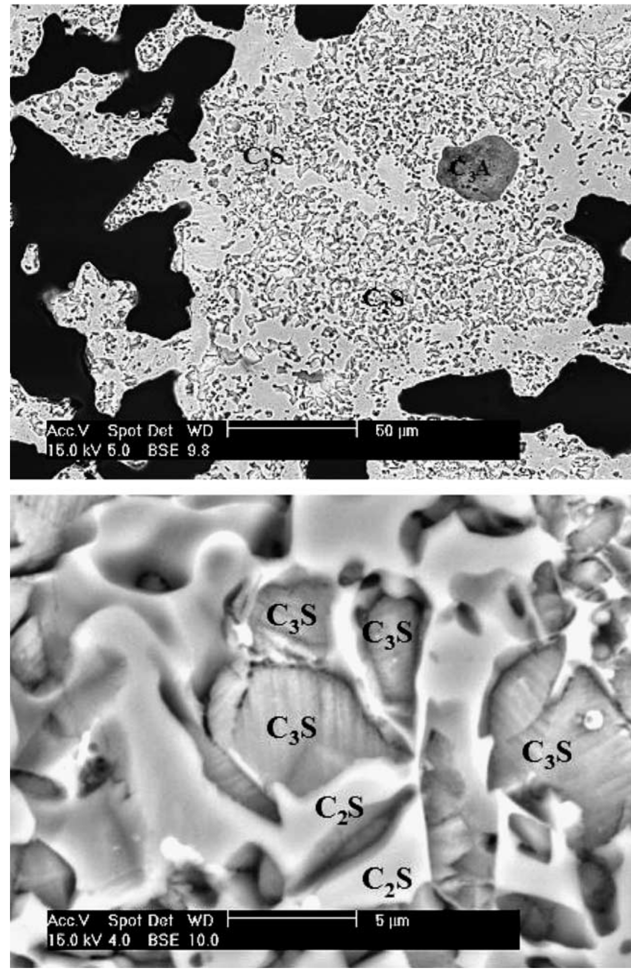

Fig. 11. Scanning electron microscope for the blend after heating to 1300 °C.

4. Conclusions

Oil shale ash can be utilized in the manufacturing of Portland cement clinkers. It does not only provide the energy source for the clinkering reactions, but the oil shale ash, which is normally a high proportion, can also be used as a blend of Portland clinker raw materials.

Up to 16% of oil shale ash can be used with a typical Portland cement clinker without affecting the main properties of the Portland clinker. The addition of oil shale ash will reduce the required clinkering temperature to around 1300 °C (Fig. 11) instead of the typical one of 1450–1500 °C. At this temperature, the clinker will have enough liquid phase to undergo the clinkering reactions.

A blending ratio of 16% oil shale ash, 18% kaolinite, and 66% calcite is suggested in this study to maximize the benefits of utilizing the Jordanian oil shale. A corresponding temperature of 1300–1350 °C is also suggested for that bending ratio.

Further experimentations are required to test the typical properties of Portland cement generated from that clinker. These tests should focus on the setting time, strength, and durability, etc.

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