

A THERMODYNAMICS STUDY ON THE UTILIZATION OF JORDANIAN OIL SHALE IN THE CEMENT INDUSTRY

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Oil shale can be utilized in manufacturing Portland cement. In addition to the utilization of the spent oil shale after combustion, it can also reduce the required temperature for clinkering reactions. A study of Jordanian oil shale was performed to maximize the use of oil shale in the cement industry. As much as 15% of Jordanian oil shale can be used with the typical cement-making raw materials without significantly altering the properties of the cement. The corresponding temperature for this ratio was found to be around 1300 °C. An optimized blending ratio of 22% oil shale, 25% kaolinite, and 53% calcite was also determined. The optimum operating temperatures for this ratio were found to be between 1300 and 1350 °C.

Introduction

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

The high percentage of ash in 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 the shale at 600 °C in concrete mixes without significantly affecting its compressive strength. However, the cementaceous properties of the spent oil shale are relatively poor. This could be explained by the low proportions of tricalcium

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silicate (C_3S) and calcium orthosilicate (C_2S) as will be discussed later in this study. Khedaywi *et al.* [3] performed a 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 commercial pozzolanic cement. In different studies of Israeli oil shale [4, 5], it was concluded that the structure and the properties of the spent Israeli oil shale are similar to that of ordinary Portland cement.

Although there are number of studies on using spent oil shale in the concrete industry, little information is available on utilizing the oil shale itself in the production of cement as an energy source for the clinkering reactions, and as a raw material to make up the cement clinker. Moreover, very little information, if any, is available on the thermodynamic reactions that occur when utilizing the oil shale in the production of cement.

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 cement clinker. This study utilizes theoretical thermodynamic equilibrium calculations as well as experimental verifications of these calculations.

Experimental

Materials

Oil Shale

Oil shale samples were obtained from the El-Lajjun deposit in Jordan. The main constituents of the oil shale in this study are as follows, 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.

Samples of laboratory ashes from this oil shale were prepared by crushing the oil shale to $<150\ \mu\text{m}$, and ashing in a laboratory furnace in accordance with the Australian Standards for ashing hard coal [6]. A known mass of oil shale is heated in air to $500\ ^\circ\text{C}$ in 30 minutes, from $500\ ^\circ\text{C}$ to $815\ ^\circ\text{C}$ in 60 minutes, and kept at $815\ ^\circ\text{C}$ for 3 hours. The particle size distribution of the ash is presented in Fig. 1. A typical analysis of an oil shale ash as determined by the X-ray fluorescence (XRF) is as follows, 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. Crystalline components were also determined by X-ray diffraction (XRD) (Fig. 2). 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 provides an approximate analysis of the main components present in the ash, wt%: anhydrite 15.9; quartz 23.0; kaolinite 17.5; magnetite 3.1; lime 38.1.

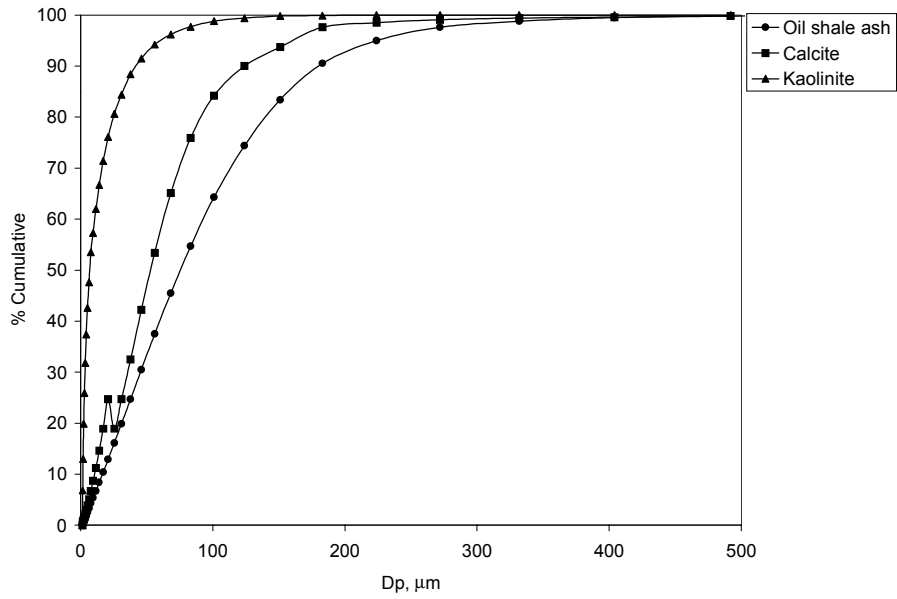


Fig. 1. Particle size distributions for samples of oil shale ash, calcite, and kaolinite used in this study

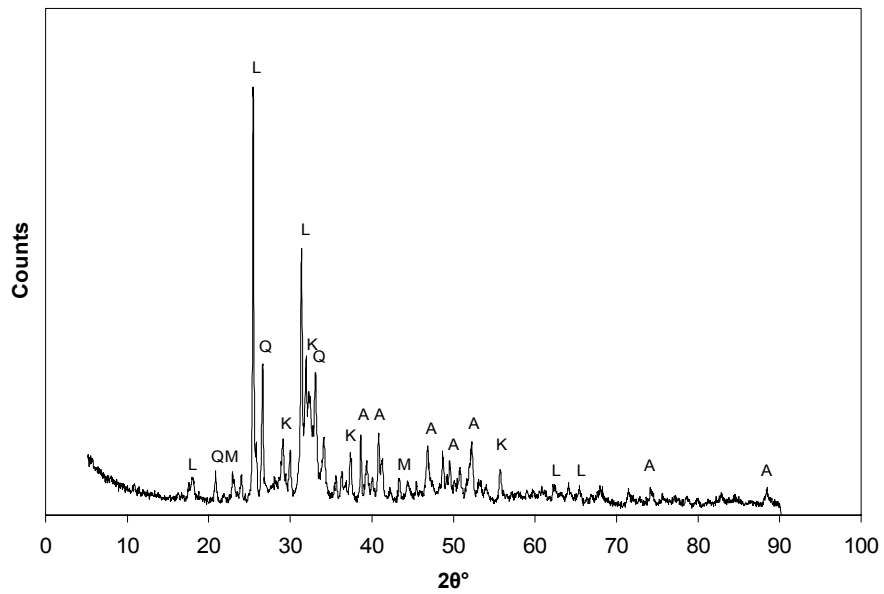


Fig. 2. XRD for the El Lajjun oil shale ash: A – anhydrite, K – kaolinite, L – lime, M – magnetite

Ordinary Portland Cement

A sample of an ordinary Portland cement (OPC) was blended with oil shale ash at different temperatures. The oxide analysis of this sample is as follows, wt%: SiO₂ 23.6; Al₂O₃ 5.9; Fe₂O₃ 2.3; CaO 65.3; MgO 1.53; Na₂O 0.1; P₂O₅ 0.1; K₂O 0.4.

Calcite and Kaolinite

Samples of naturally occurring calcite and kaolinite were used in the study. The percentage of CaCO₃ in the calcite sample is around 97%, with clays and quartz impurities. Kaolinite is similar in purity with few percent of calcite and other clays. The particle size distribution for the calcite and the kaolinite samples used in this study is shown in Fig. 1.

Thermodynamic Calculations

Thermodynamics calculations were performed using F.A.C.T., a computer program, 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 Bale *et al.* [7]). A comprehensive study for the system Al–Ca–Fe–O–Si for coal ash was presented by Jak [8].

F.A.C.T. calculations were used in this study to predict the quantities of tricalcium silicate (3CaO·SiO₂, C₃S), calcium orthosilicate (2CaO·SiO₂, C₂S), tricalcium aluminate (3CaO·Al₂O₃, C₃A), and tetracalcium aluminoferrate (4CaO·Al₂O₃·Fe₂O₃, C₄AF) at different temperatures. These minerals are the most important constituents in Portland cement. F.A.C.T. was also used to estimate the quantities of liquid present at different temperatures.

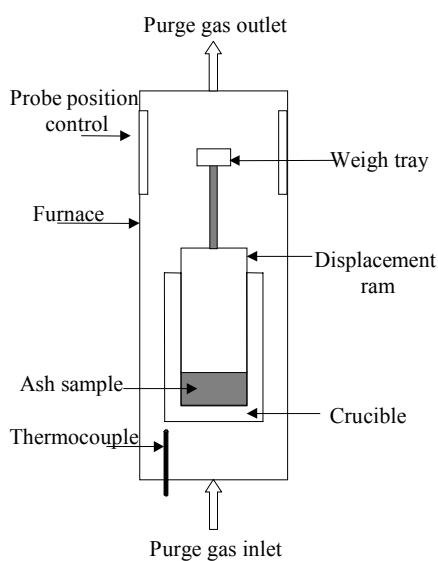


Fig. 3. Schematic diagram of a thermomechanical analysis set-up

Thermomechanical Analysis

Thermomechanical analysis (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 F.A.C.T calculations. In this experiment, around 50-mg sample of ash was initially compressed to 0.35 MPa in a molybdenum crucible. The 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 temperature to 1600 °C at 5 °C/min. TMA experiments were conducted in argon atmosphere in order to prevent oxidation of the molybdenum crucible. Figure 3 shows the crucible set-up in the TMA.

Results and Discussion

Figure 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 cement, 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 amount 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 and the large quantity of calcium sulphate that are present in the sample. As shown in Fig. 5, the amount of lime to form CaO should be from around 65 to 75%. A small amount of α - C_2S starts to precipitate out of the liquid slag above 1450 °C.

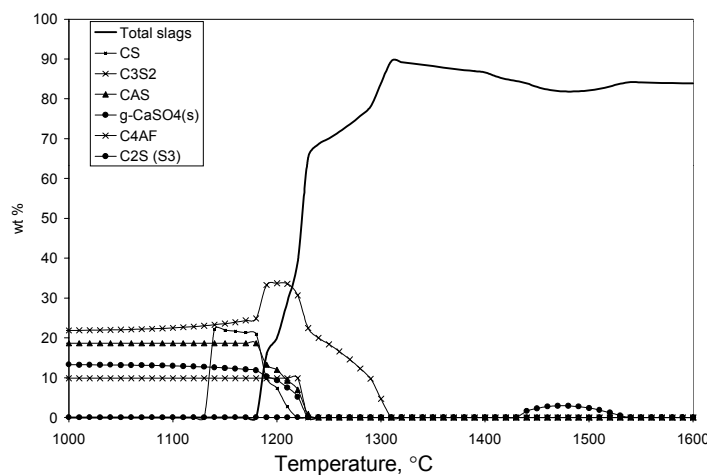


Fig. 4. Thermodynamic equilibrium diagram for oil shale ash

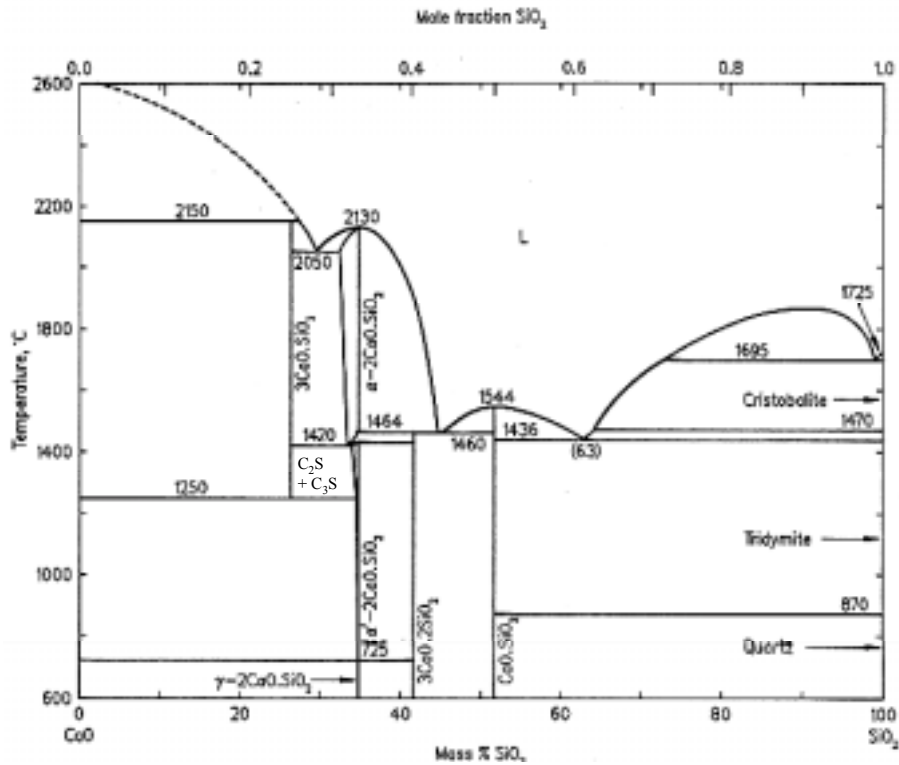


Fig. 5. Phase diagram of the system CaO-SiO₂ [12]

Different blending ratios between oil shale ash and ordinary Portland cement were used in this study to determine the possible blending ratio with normal clinker raw materials for further processing without affecting the properties. Figure 6 shows the minerals that exist, at different temperatures, when blending oil shale ash with ordinary Portland cement. It also shows the amount of liquid glass at every temperature as calculated by the F.A.C.T program. At 1250 °C, neither the cement nor the ash blends would be a suitable clinker material. This is due to the very low amount of C₃S, which is essential to make up the early strength of concrete. C₃S is reported to be stable at temperatures between 1300 and 1800 °C [10]. At temperatures above 1250 °C and below 1420 °C, the C₂S and C₃S are in equilibrium (Fig. 5).

At temperatures between 1300 and 1350 °C, it is clear that a blending ratio of 10 to 15% could be used in making clinker materials. This is due to the formation of relatively higher amounts of C₃S and C₂S, in addition to the C₄AF and C₃A. Unlike the cement at those temperatures, the mentioned blend contains enough liquids to proceed with the clinkering reactions during the process of making cement. It is reported by many researchers that the minimum required amount of liquid required for the clinkering reactions is around 20% [10].

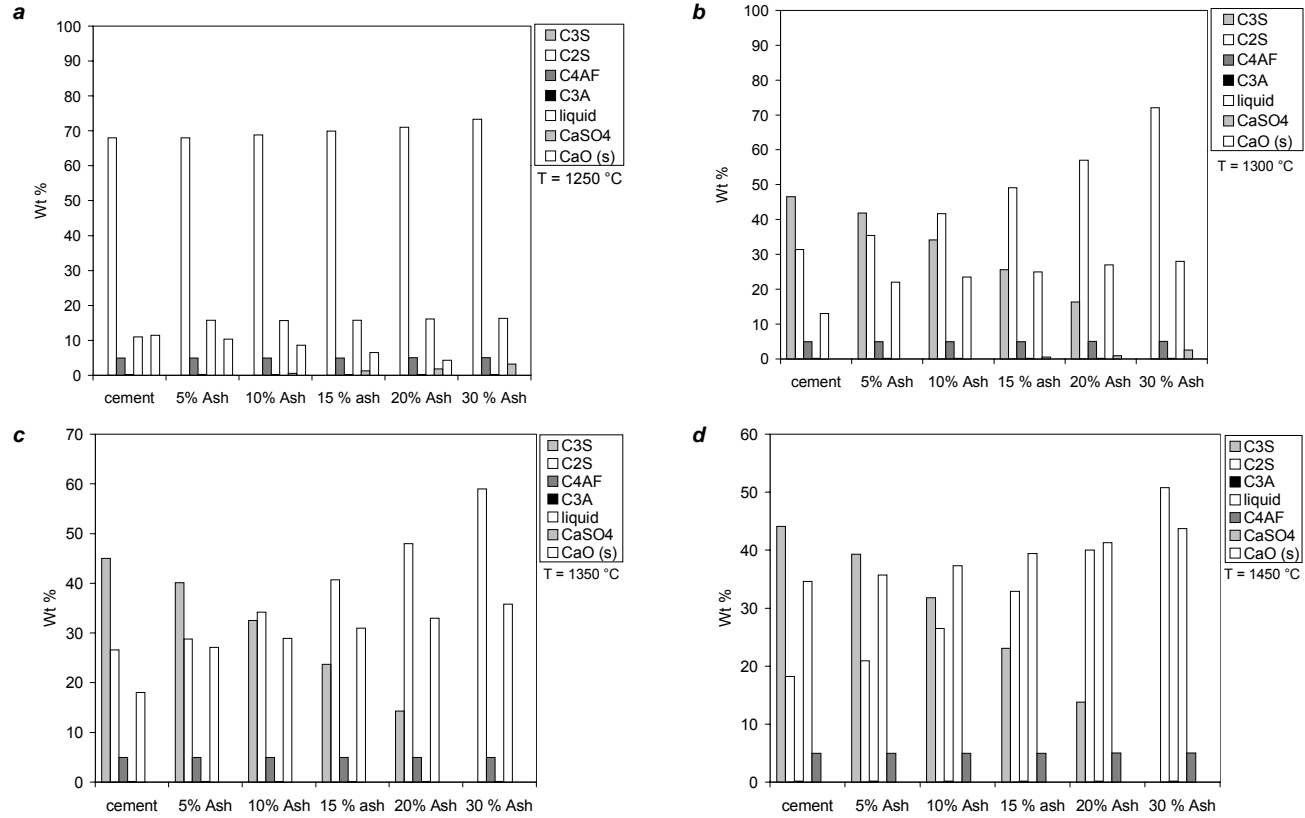


Fig. 6. Main clinker minerals, and liquid phase present after blending oil shale ash with Portland cement at 1250 (a), 1300 (b), and 1350 (c), and 1450 °C (d)

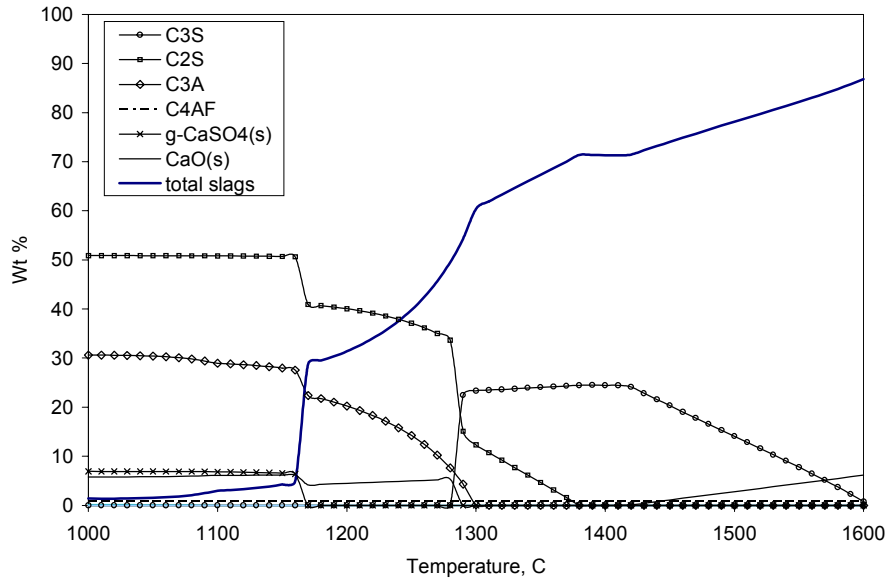


Fig. 7. F.A.C.T calculations for the main species present when blending 22% oil shale, 25% kaolinite, and 53% calcite

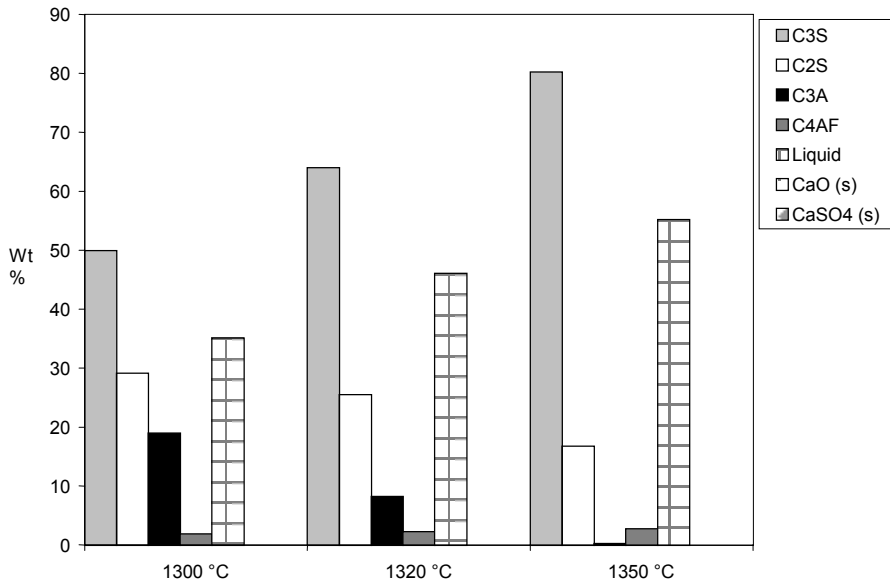


Fig. 8. Proportion of main clinker components from blending of 22% oil shale, 25% kaolinite, and 53% calcite

Different blending ratios of oil shale ash, calcite and kaolinite, which are considered the main raw materials used for manufacturing cement, were tried using F.A.C.T. calculations to come up with constituents close to Portland cement. The optimized ratio obtained was 22% of oil shale, 25% kaolinite, and 53% of calcite.

Figure 7 shows the main species that are present at different temperatures when using the above-mentioned blending ratio. Significant melting of the constituents occurs above the temperature of 1150 °C, and the solid CaSO_4 participates in the melting process. As mentioned earlier, the C_3S starts to form above 1300 °C. Further heating results in lowering the quantity of C_2S , which participates in the formation of the liquid phase.

The species that exist for different ratios is shown in Fig. 8. It is clear that a temperature of 1300 to 1350 °C can be used for a blending ratio that makes up all the necessary components of cement clinkers. The variation in temperature would result in a difference in the performance of the resulting cement. It is important here to mention that at those temperatures the clinker would have enough liquid phases to perform the clinkering reactions.

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 cement. The difference in the ratio of C_3S and C_2S will affect the setting time of the concrete as well as the initial strength. However, all the above-mentioned ratios are considered among the standards of ordinary Portland cement.

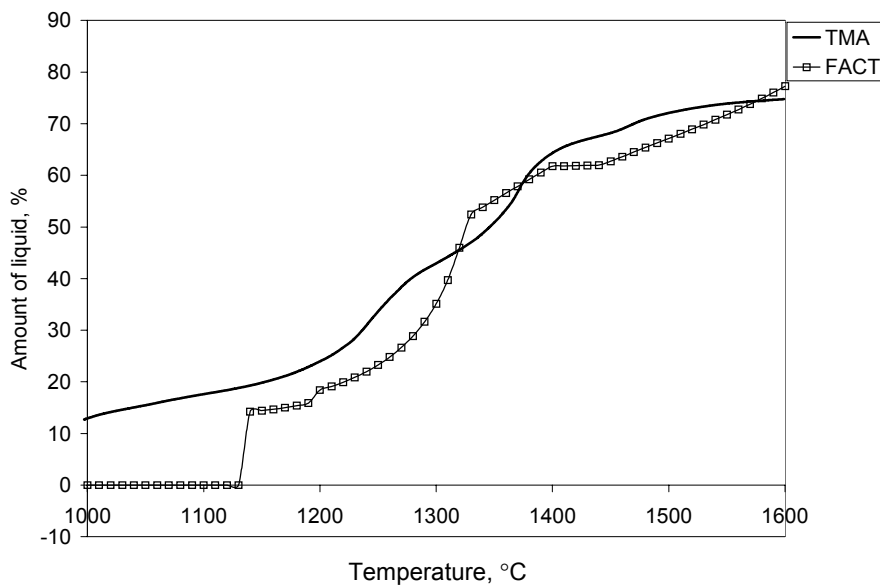


Fig. 9. Comparison between the quantities of liquid phases obtained by F.A.C.T. calculations, and the TMA trace (shrinkage) obtained for the blend of 22% oil shale, 25% kaolinite, and 53% calcite

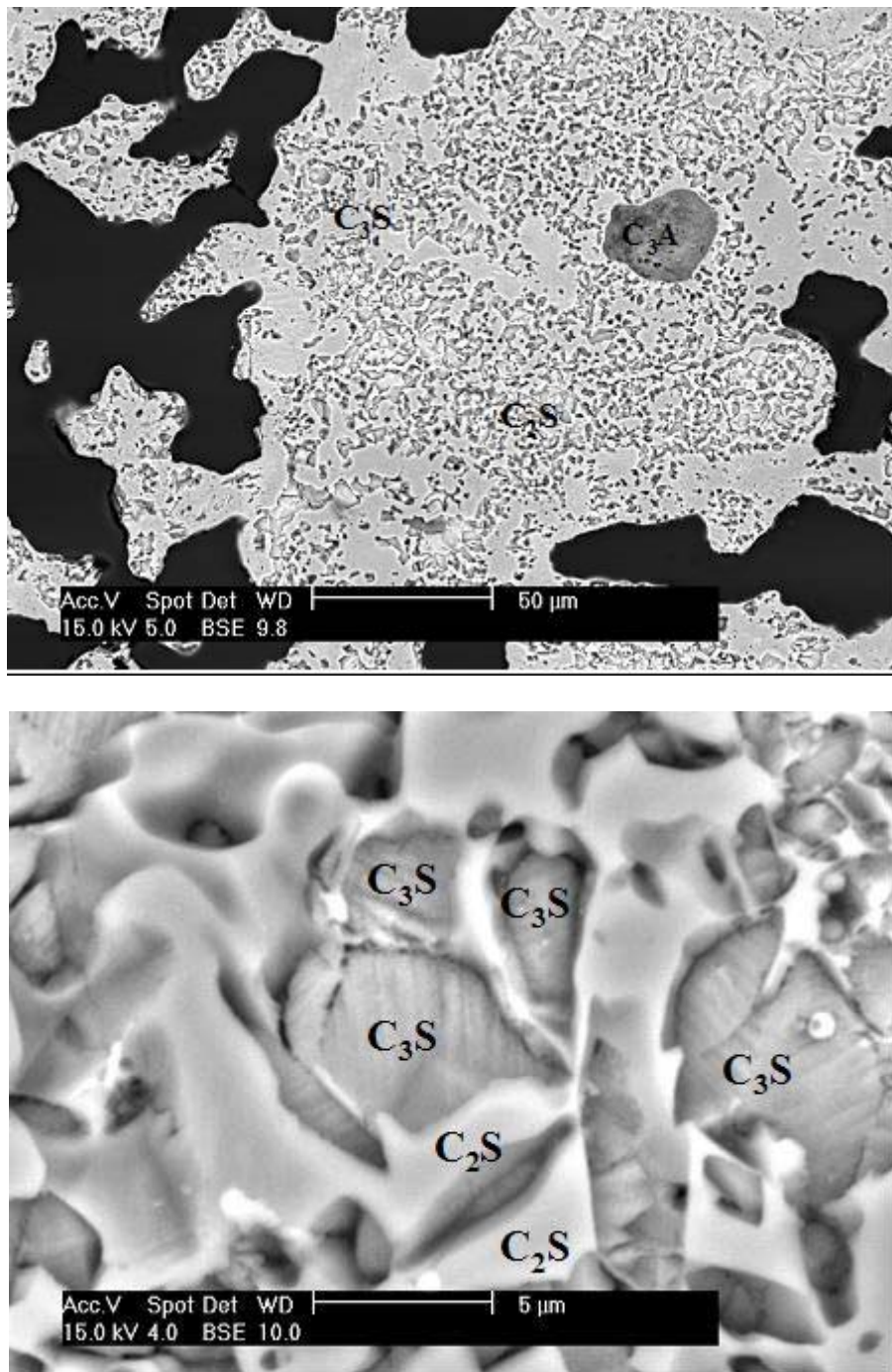


Fig. 10. Scanning electron microscope images for the blend after heating to 1300 °C

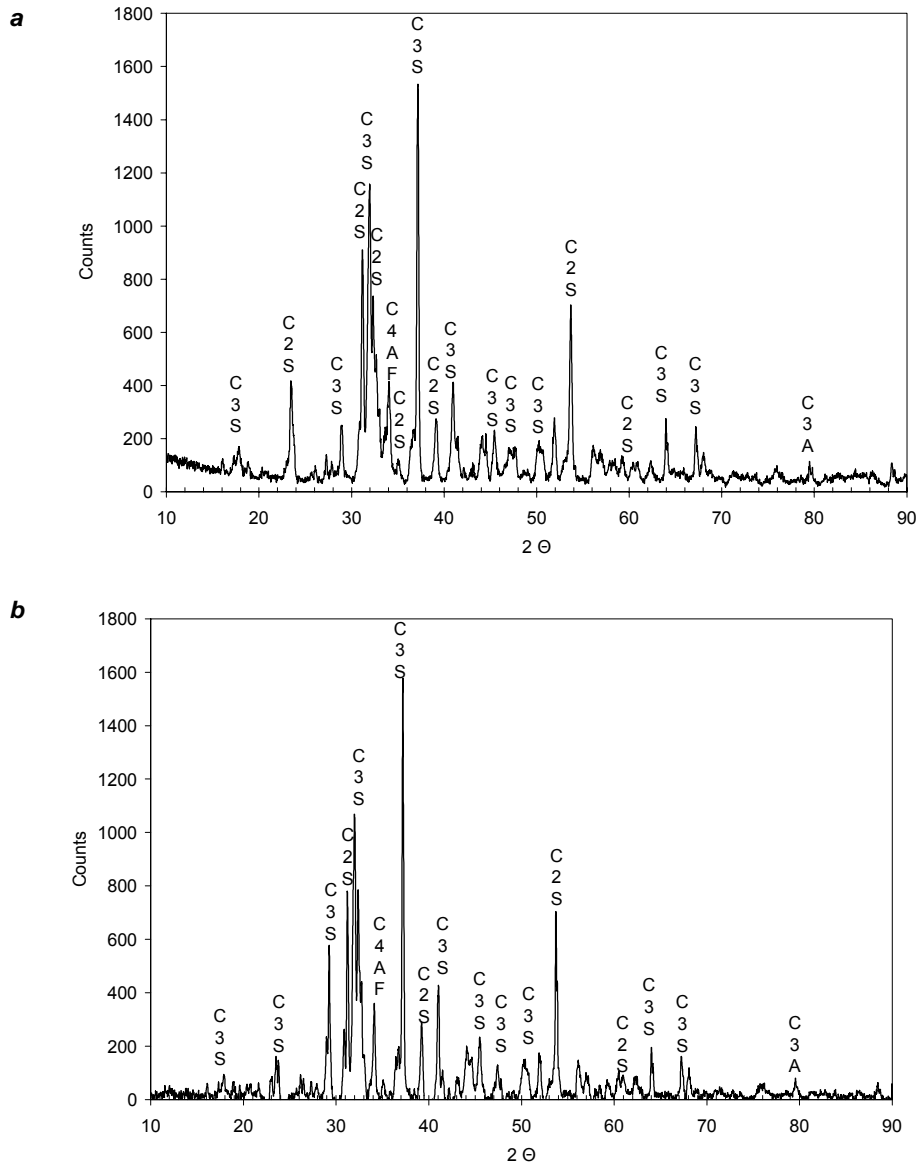


Fig. 11. X-ray diffraction analyses for the suggested blend of oil shale, kaolinite, and calcite at 1300 (a), and 1350 °C (b)

Thermomechanical analysis for the suggested blend ratio was performed in order to verify the amount of the liquid phase obtained from F.A.C.T calculations. Figure 9 shows a close profile of the liquid formed at different temperatures, particularly at temperatures higher than 1100 °C. Below this temperature sintering is suspected to have occurred which resulted in shrinkage of the pellet. That would result in further reduction in the height of the pellet of the blend. (Further details about sintering by TMA are available elsewhere, Al-Otoom *et al.* [11]).

Scanning electron microscopic images were obtained for the suggested blend at 1300 °C. Energy Dispersive Spectrum analyses were also obtained for this blend. These analyses show that C_3S , and C_2S are the dominant species present. Figure 10 presents examples of these phases. Similar results were obtained from XRD analyses of samples heated to 1300 and 1350 °C (Fig. 11).

Conclusions

Oil shale ash can be utilized in the manufacturing of 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 clinker raw material.

Up to 15% of oil shale ash can be used with a typical Portland cement clinker without affecting the main properties of the cement. The addition of oil shale will reduce the required temperature to around 1300 °C instead of the typical 1450–1500 °C. At this temperature, the clinker will have enough liquid phase to undergo the clinkering reactions.

A suggested blending ratio of 22% oil shale, 25% kaolinite, and 53% calcite is suggested by 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 experiments are required to test the typical properties of cement generated from that suggested blending ratio. These tests should focus on concrete strength and durability from an engineering point of view.

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