ENERGY REQUIREMENTS OF USING OIL SHALE IN THE PRODUCTION OF ORDINARY PORTLAND CLINKER

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Energy balance was performed on the clinkering process when utilizing oil shale as a source of both raw materials and energy. The balance was also compared with the typical energy requirements for production of Ordinary Portland (OP) Clinker. The use of Jordanian oil shale can reduce energy requirements in production of OP clinker by 15–20%. This reduction is due to two factors: lower clinkering temperature of 1300–1350 °C and an appropriate proportion of the proposed raw materials. An additional energy of 1726 kJ/ton clinker, which represents 45% of the required energy, is needed to achieve the required clinkering temperature. This could be achieved by estimating the amounts of makeup fuel basing on the net calorific value of this fuel.

Introduction

Cement industry is known to consume a large share of the total industrial use of energy and it is estimated at 30-40% in some countries [1]. Different sources of energy have been utilized either in the form of electrical power or in the form of thermal energy. The amount of energy consumed in the production of OP clinker ranged from 3000 to 6000 kJ/kg clinker depending on the type of process and raw materials [2].

Coal, heavy oil, and natural gas are used as thermal energy resources for production of cement clinker. Other fuels like oil shale and biomass may also be used. Although oil shale is considered one of the largest potential energy resources in the world, its use in the production of clinker is still limited.

Soaring prices of oil have led many investors to consider oil-alternative energy resources. The oil equivalent of oil shale around the world is estimated to be about 30 times the reserve of crude oil [3]. Jordan possesses

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large oil shale deposits, which are located in several areas mainly in El-Lajjun, Sultani, Jurf Eddarawish, Wadi Mgher, and Khan Ez-Zabib.

Commercialization of oil shale in the form of oil is being studied. 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 [4]. Cementing properties of oil shale on its own have been found earlier to be poor [5]. A recent study has been completed to study the thermodynamics of proportioning oil shale with other cement raw materials [6]. The study showed that oil shale ash can be used with the following proportions; 16% oil shale ash, 18% clay, mainly kaolinite, and 66% calcite. The study also confirmed that a lower clinkering temperature (1300–1350 °C) is required to produce OP clinker. This in part is capable of reducing the amount of energy and thus the cost of producing OP clinker.

This work is a part of an ongoing research on utilization of the Jordanian oil shale in the production of OP clinker. The study aims to find the energy requirements for the above mentioned blending ratio. It also aims to find the amount of additional heat required in addition to the heat generated from combustion of oil shale.

Methodology

Production of OP clinker

Material balance

Material balance is performed initially on production process of OP clinker using the typical chemical composition of minerals in OP clinker: (mass %) C_3S – 45; C_2S – 25; C_3A – 22; C_4AF – 8. From these proportions the amount of CaO and hence the amount of $CaCO_3$ are determined. Using a similar methodology, the amounts of kaolinite, and silica were calculated. A full description of this methodology is explained below [7]:

$$Total\ moles\ of\ CaO\ required = 3\ moles\ of\ C_3S + 2\ moles\ of\ C_2S$$
$$+ 3\ moles\ of\ C_3A + 4\ moles\ of\ C_4AF \tag{1}$$

$$Total\ moles\ of\ CaCO_3\ required = total\ moles\ of\ CaO \tag{2}$$

$$Total\ moles\ of\ Fe_2O_3\ required = moles\ of\ C_4AF \tag{3}$$

$$Total\ moles\ of\ Al_2O_3 = moles\ of\ C_4AF + moles\ of\ C_3A \tag{4}$$

$$Moles\ of\ kaolinite\ required = total\ moles\ of\ Al_2O_3 \tag{5}$$

$$Moles\ of\ free\ SiO_2\ required = moles\ of\ C_3S + moles\ of\ C_2S$$
$$- 2\ moles\ of\ kaolinite, \tag{6}$$

where
C_3S tricalcium silicate($3CaO \cdot SiO_2$)
C_2S dicalcium silicate ($2CaO \cdot SiO_2$)

C$_3$A   tricalcium aluminate (3CaO·Al$_2$O$_3$)

C$_4$AF   tetracalcium aluminoferrite (4CaO·Al$_2$O$_3$·Fe$_2$O$_3$)

Energy balance

Energy balance was performed utilizing the calculated amounts of CaCO$_3$, clay, and kaolinite in the raw materials. All processes in the production of clinker are divided into hypothetical paths as shown in Fig. 1. All of these hypothetical paths are considered basing on the main transformations that happen to the OP raw materials [7]. On a basis of 1 ton of OP clinker produced at 1450 °C, the amount of required energy has been calculated by adding all enthalpies of all hypothetical paths drawn:

$$Q = \overset{Paths}{\sum} M \cdot \Delta H_{Sens} + \overset{Paths}{\sum} N \cdot \Delta H_{rxn} + \overset{Paths}{\sum} N \cdot \Delta H_{m}, \qquad (7)$$

where M is the mass of component (kg), and N is mole of component.

The sensible heat (ΔH^{*}_{sens}) of all species is calculated using

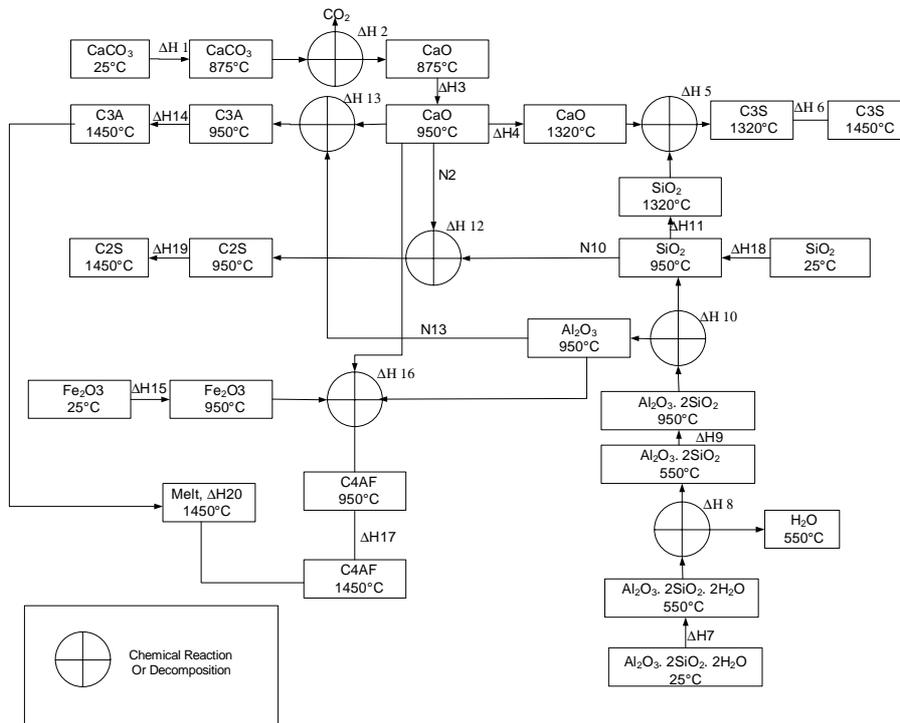$$\Delta H_{Sens} = M \int\limits_{T1}^{T2} cpdT. \qquad (8)$$

Fig. 1. Schematic diagram of hypothetical paths in OP clinker production.

The heat of reaction (ΔH^{*}_{rxn}) was calculated from the difference between the heat for formation of the products and the reactants:

$$\Delta H^{*}_{rxn} = \sum_{products} \Delta H^{*}_{f} - \sum_{reactants} \Delta H^{*}_{f} . \qquad (9)$$

The thermodynamic data used in this study are summarized in Table 1 and Table 2.

The heat of melting and the proportions of melt were found using the software of Facility for the Analysis of Chemical Thermodynamics (FACT). A full description of the above mentioned software is described elsewhere [8, 9]. The heat of melting obtained by FACT was compared with the values given in the literature and found to be approximately 44 kJ/mol of melt [7].

Table 1. **Thermodynamic data for raw materials and clinker compounds**

Compound	Heat of formation, ΔH^{o}_{f}, kJ/mol [11–13]	Cp, kJ/kg·K [12]
$CaCO_3$	−1207	$1.04+2.19\times10^{-4}T-2.6\times10^{-2}T^{-2}$
CaO	−635	$0.886+1.01\times10^{-4}T-1.1\times10^{-8}T^{2}$
Fe_2O_3	−822	$0.954-8.02\times10^{-5}T+3.72\times10^{-8}T^{2}$
SiO_2	−908	$1.21+2.16\times10^{-5}T-6.89\times10^{4}T^{-2}$
Al_2O_3	−1669	$1.13+1.52\times10^{-4}T-2.02\times10^{-8}T^{2}$
CO_2	−393	$0.82+9.62\times10^{-4}T-6.56\times10^{-7}T^{2}$
$Al_2O_3\cdot2SiO_2\cdot2H_2O$	−4120	$1.105+8.38\times10^{-4}T-4.3\times10^{-7}T^{2}$
$Al_2O_3\cdot2SiO_2$	−2578	$1.19+6.3\times10^{-5}T-6.68\times10^{-9}T^{2}$
$H_2O(g)$	−241	$1.85+3.8210^{-4}T+4.22\times10^{-7}T^{2}$
C_2S	−2308	$0.784+2.68\times10^{-4}T$
C_3S	−2931	$0.916+1.58\times10^{-4}T-1.87\times10^{4}T^{-2}$
C_3A	−3561	$0.930+4.88\times10^{-4}T-7.68\times10^{4}T^{-2}$
C_4AF	−5080	$3.25+1.504\times10^{-4}T-7.52\times10^{2}T^{-2}$

Table 2. **Reactions and decomposition processes occurring at clinker production**

Reaction	T, ^{o}C	ΔH_{rxn}, kJ/mol
$CaCO_3 \rightarrow CaO + CO_2$	875	16
$3CaO + SiO_2 \rightarrow C_3S$	1300	−173
$Al_2O_3\cdot2SiO_2\cdot2H_2O \rightarrow Al_2O_3\cdot2SiO_2 +2 H_2O$	550	1049
$Al_2O_3\cdot2SiO_2 \rightarrow Al_2O_3 + 2SiO_2$	950	−784
$2CaO + SiO_2 \rightarrow C_2S$	950	−186
$4CaO + Fe_2O_3 + Al_2O_3 \rightarrow C_4AF$	950	−19

Production of OP clinker with oil shale

Material balance

Material balance is performed when utilizing the ratios of blending 16% oil shale ash, 16% kaolinite, and 66% calcite. The amounts of C_3S, C_2S, C_3A, and C_4AF have been calculated and compared with the amounts found by FACT in the previous study. The proportions of the above compounds obtained by FACT are shown in Fig. 2.
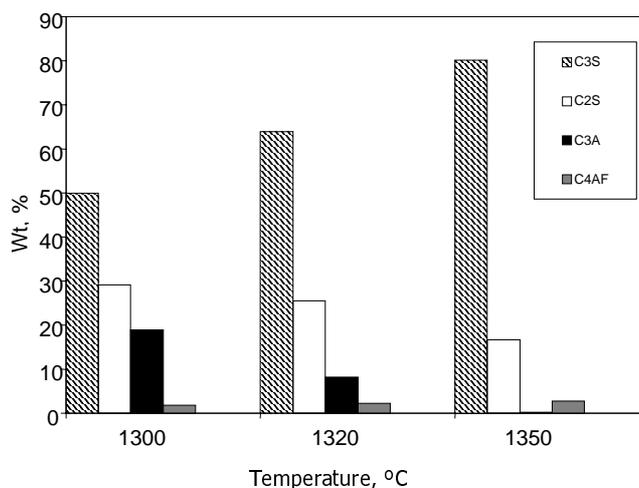

Fig. 2. Proportions of clinker compounds when utilising oil shale as OP raw material [6].

Energy balance

Energy balance was performed using a method similar to that described above. However, since the maximum temperature is 1300–1350 °C, the hypothetical paths are slightly different from the above paths and shown in Fig. 3.

Results and discussion

Material and energy balance for OP clinker

Based on typical values of clinker mineral composition given above, raw materials that constitute this clinker have been calculated by stoichiometric proportioning. The raw materials required for 100 gram clinker (g/100 g clinker): $CaCO_3$ – 119.3; $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ – 25.26; SiO_2 – 17.62; Fe_2O_3 – 2.63, total – 164.8. It is noted that the total mass of the raw material is greater than the mass of the final product since decomposition reactions of $CaCO_3$ and $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ release CO_2 and H_2O, respectively, into the gaseous phase. Therefore, the remaining solids shall add up to 100 grams of clinker.

Energy balance on transformation of raw materials in typical proportions of clinker is explained in Fig. 1. This figure is based on dividing these transformations into small and simpler hypothetical paths in series and in parallel in order to account for all reactions and heating processes during the production of clinker. The heat of reaction has been calculated from the difference between the heat of formation of the products and that of the reactants at reaction temperatures. A summary of the heats of reactions involved in the production of clinker is also given in Table 2.

The value resulted from adding up the summation of all the heats of the hypothetical paths is approximately 4100 kJ/ton clinker. This value is within the average value for the heat requirement for the production of Portland clinker [2].

Material and energy balance for using oil shale to produce OP clinker

Previous study on thermodynamics suggested that the use of 16% oil shale ash, 18% kaolinite, and 66% calcite would produce similar proportions of OP clinker [6]. The composition of oil shale mineral matter is as follows (wt.%): $CaCO_3 - 38.1$; $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O - 17.5$; $SiO_2 - 23$; $CaSO_4 - 15.9$; $Fe_2O_3 - 3.1$, while final composition of the proposed raw materials blend with this oil shale is (mass g per 100 g clinker): $CaCO_3 - 128.7$; $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O - 24.2$; $SiO_2 - 3.7$; $CaSO_4 - 2.5$; $Fe_2O_3 - 0.5$; total – 159.6. These proportions were found to be produced at temperatures starting from 1300 °C. This temperature is 150 °C less than normal operating temperature of OP clinker. Figure 2 shows these proportions at different temperatures.

Material balance calculations started from the above suggested proportions to find all intermediate and final compositions of OP clinker. The composition of final clinker (mass %, $C_3S - 53$; $C_2S - 25$; $C_3A - 19$; $C_4AF - 3$) is within normal specifications of OP clinker and similar to that obtained in the previous study as shown in Fig. 2 [6].

Energy balance calculations were performed using a method similar to that mentioned before. Figure 3 shows the steps of the hypothetical paths when utilizing oil shale. This procedure was repeated at final temperatures of 1320, 1335, 1350, and 1450 °C in order to compare the energy requirements when using Jordanian oil shale in the production of clinker.

Operating at the suggested temperatures found in previous studies (1300–1350 °C [6]) has shown an energy saving of around 15–20%, as shown in Fig. 4, which reflects great savings in the energy cost. This reduction of energy is believed to occur as a result of formation of low eutectic temperatures when using oil shale. The initial composition of clinker raw material differs when using oil shale. This composition slightly differs from normal composition of OPC. Energy requirements when using oil shale with the determined blend at the same operating temperature as the typical clinker production temperature (1450 °C) has also resulted in energy saving by approximately 15%. This reflects that the energy saving does not only come

from reducing the operating temperature, but it also comes from the optimized raw material blend when using oil shale.
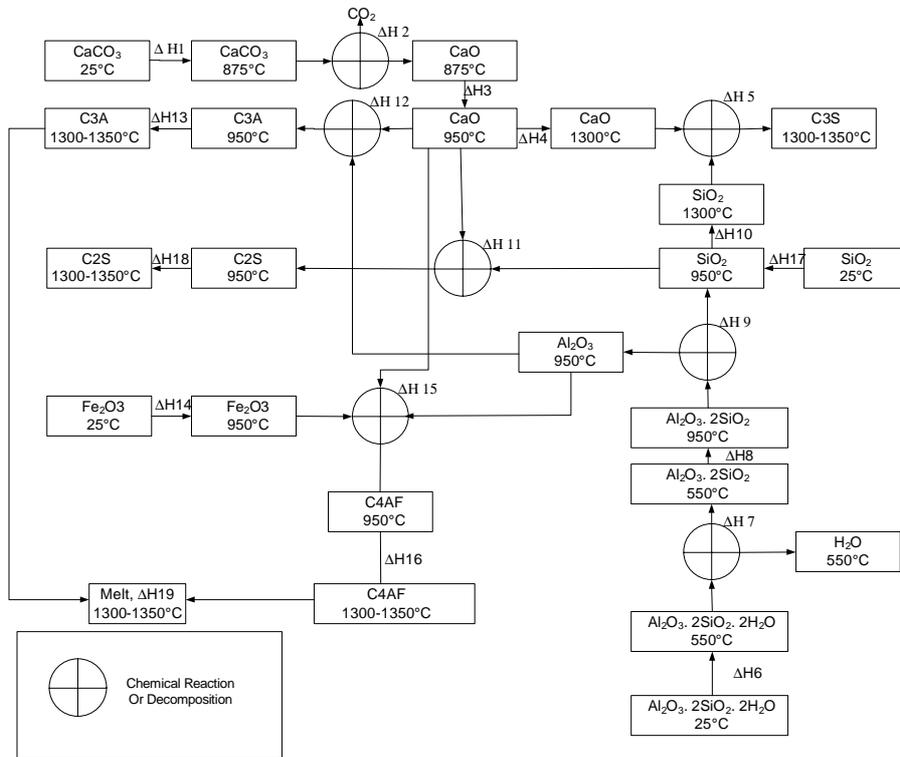

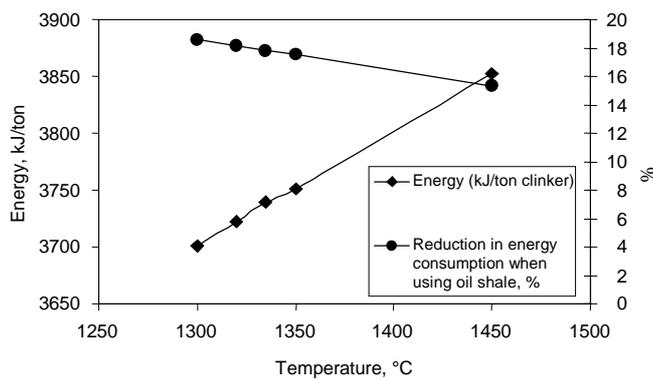*Fig. 3.* Schematic diagram of hypothetical paths in OP clinker production when utilizing oil shale.

Fig. 4. Energy requirements and reduction in energy use when utilizing oil shale in the production of OP clinker.

One of the largest deposits of oil shale in Jordan is the El-Lajjun deposit. Ash content of this oil shale is 54%. Therefore, when using 16% oil shale ash in the raw material blend, this corresponds to using 296 kg of oil shale per ton of clinker. Since the calorific value of El-Lajjun oil shale is 6906 kJ/kg [10], the amount of energy that can be used is 2044 kJ/ton of clinker. The average heat requirements for clinkering blends with oil shale at 1300–1350 °C are 3770 kJ/kg, therefore, additional heat of 1726 kJ/kg or 45% additional energy is needed.

Conclusions

This work is a part of an ongoing work to determine energy requirements for production of OP clinker when utilizing local oil shale. This was achieved by performing energy balance on the clinkering process by dividing all processes into hypothetical paths and the changes in enthalpy were calculated for each of these paths.

When utilizing oil shale in the proposed blend (16% oil shale ash, 18% kaolinite, and 66% $CaCO_3$), there would be an energy savings of 15–20% owing to the nature of the raw materials used and low clinkering temperatures required (1300–1350 °C). This low temperature can be achieved since the eutectic temperature of the proposed blend with oil shale is low. The formation of a significant amount of liquid phase during clinkering is extremely important. This significant amount can only be achieved at temperatures higher than 1400 °C in a typical OP clinker. While, when using oil shale, a significant amount of liquid has been achieved at temperatures of 1300–1350 °C [6].

The composition of the resulting clinker when using oil shale in the blend is slightly different from the average composition of the OPC. Although the final properties of the cement would slightly differ from the average composition of OP clincker, the new composition ratios obtained when using oil shale are within acceptable limits of OP clinker.

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