



Characterization of Timahdit oil shale for the use of their ash as a raw material for the preparation of a clinker

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Abstract

In this research, the mineral and the mineralogical composition of Timahdit oil shale ash (OSA) were followed by fluorescence (XRF), X-ray diffraction (XRD) and their morphology by scanning electron microscopy (SEM). The XRF and XRD showed respectively that the mineral composition of OSA composed mainly SiO₂ and CaO with average amount of Al₂O₃ and other minor oxide and the main crystalline phases present were quartz, wollastonite, gehlenite, anhydrite, periclase and akermanite. The scanning electron microscopic analysis (SEM) have permitted to observe the morphology of the particles that exist in the oil shale calcined at 900°C and hydrated for half an hour. The physic-chemical characteristics of three types of clinkers were studied.

- The clinker (1) prepared in the normal processes involved in Asment plant Temara (CIMPOR).
- The clinker (2) produced in the laboratory with the same raw materials as that of ordinary Portland clinker.
- The clinker (3) produced in the laboratory using oil shale ash in the raw materials.

The results of chemical compositions of the three clinkers given by XRF showed that their major oxides are similar to those of an Ordinary Portland clinker. For the prepared clinkers the major phases are also those of an ordinary clinker (C₃S, C₂S, C₃A and C₄AF). The same analysis for the three days hydrated clinker (3) allowed us to observe the reduction of alite peaks and the appearance of C-S-H, CaCO₃, Ca(OH)₂, C₄AH₁₃ and C₃AH₄ and DSC allowed us to observe the endothermic behaviour of the clinker (3) hydrated for 3 days.

Keywords: Oil shale ash, clinker, heat treatment, hydration, DRX, FRX, SEM and DSC.

Introduction

In the field of building and construction, the remarkable properties of additives to cement allow their use in many important applications. These additives are industrial wastes used to replace a part of the clinker in cement production. They represent an interesting economic and environmental topic of research because of their ability to reduce the amount of required clinker, which lowers the production costs, the energy consumption and the polluting emissions related to the manufacture of Portland cement.

The objective of this study is to assess the relevance and anticipated the impact of the use of Timahdit oil shale in the starting material of clinker preparation. Timahdit is one of the most important and the most studied deposit of Morocco. It is located approximately at 240 km of the capital Rabat. These oil shales are sedimentary rocks containing organic matter continental or marine origin [1]. Their organic matter is finely disseminated in the inorganic fine mineral matrix [2.3]. The theoretical level of this reserve is estimated by ONHYM to a dozen of billion barrels [4].

2. Materials and methods

Oil shales used in this study were donated by the National Office of Hydrocarbons and Mines (ONHYM). They were extracted from the sublayer M, from Timahdit deposit in blocks of several kilograms. They were crushed and finely ground using a disc Mixer Mill (Siebtechnik).

The raw materials used for the preparation of three various clinkers were provided by the Asment Plant (CIMPOR) and prepared by following the same methodology applied by this factory.

2.1. Samples preparation

The Raw materials used in the preparation of clinkers (oil shale, limestone of Asment 1, limestone of Asment 2, schists of Asment and pyrrhotite ash) were extracted and crushed separately by a jaw crusher (old generation Fritsh pulverisette kind 01-703) to reduce their size by means of crushing and homogenization.

Oil shales (density = 2.6 g/cm³) samples were finely ground and then calcined in a muffle furnace at 900°C for 30 minutes. After removing these samples from the oven, they were kept in a desiccator containing silica gel to protect them against moisture and atmospheric CO₂. Limestone was also dried in an oven at 110°C for four hours.

2.2. Preparation of clinkers

Samples of the clinkers were prepared by different methods to study their physicochemical characteristics.

-The clinker (1) developed through the normal processes involved CIMPOR and this all along the process.

-The clinker (2) produced in the laboratory of the plant according to the CIMPOR process with the same content of raw materials applied by the plant. The percentages of the starting materials are presented in Table 1.

-The clinker (3) with oil shale ash as additive in the raw material. This elaborated clinker was prepared in the proportions of the CIMPOR clinker plant by a 2.5 % correction of shales Asment in the raw materials. The percentages of the various compounds in the starting materials are given in Table 2.

Table 1: Percentage of raw materials used to prepare the clinker 2

| Starting materials | Lime stone Asment 1 | Lime stone Asment 2 | Shale Asment | Ash pyrrhotite | Lime stone |
|--------------------|---------------------|---------------------|--------------|----------------|------------|
| % | 42.15 | 22.50 | 8.35 | 0.70 | 27 |

Table 2: Percentage of raw materials used to prepare the clinker 3

| Starting materials | Lime stone Asment 1 | Lime stone Asment 2 | Shale Asment | Ash pyrrhotite | oil shale calcined 900°C |
|--------------------|---------------------|---------------------|--------------|----------------|--------------------------|
| % | 30 | 54.80 | 4.8 | 1 | 15 |

2.3. Sample Hydration

The samples were hydrated according to the weight ratio water/solid = 0.5. Then, these mixtures were placed in clean beakers and stored in a humidity cabinet (20°C ± 1) until the desired age: ½ hours for OSA and 3 days for clinker 3. After the required time, the hydration of samples was stopped by washing them with acetone. This solvent was chosen for its hydrophilicity and volatile nature. Once dried, the samples were finely ground and stored in a dryer.

2.4. Determination of free lime (CaO %)

The determination of free lime is important, it depends on the product studied. It judges the quality of the clinkerisation. Its dosage was done by using the Ethylene Glycol method.

2.5. X-ray fluorescence analysis

The analysis of the chemical compositions of raw materials and the different prepared clinkers were characterized using X ray fluorescence device (a Philips PW 16660 spectrometer).

2.6. X-ray diffraction analysis

The analysis of the mineralogical compositions of the various samples were performed using a Siemens D 5000 diffractometer, using the radiation $\lambda\alpha\text{Cu} = 1.5406 \text{ \AA}$. Quantification of crystallographic phases was carried out by an X-POWDER software.

2.7. Analysis by differential scanning calorimetry

Thermal analysis of 3 days hydrated clinker (3) was performed using a DSC calorimeter SETRAM 121 equipped with a computer. The scanning analysis are performed under an inert gas to prevent the reaction of the studied materials with the furnace atmosphere.

2.8. Analysis by scanning electron microscope

The surface of the sample of oil shale calcined at 900°C and hydrated for half an hour was examined with an environmental scanning electron microscope (ESEM) Quanta™ Series, coupled to an X-ray microanalysis (EDX-detector EDAX) and a detector for backscattered electrons. This system allows giving the chemical composition of samples in a gas pressure up to 26 mbar.

3. Results and discussion

3.1. X-ray fluorescence (XRF)

The mineral composition of raw materials and OSA were analysed by the diffraction of XRF. The results (Table 3) showed the difference in oxide compositions.

Table 3: Chemical analysis of the starting materials (*LOI: loss on ignition)

| Oxydes | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | TiO ₂ | MnO | P ₂ O ₅ | *LOI |
|-----------------------|------------------|--------------------------------|--------------------------------|-------|------|-----------------|------------------|------------------|------|-------------------------------|-------|
| Limestone Asment 1 | 12.16 | 1.09 | 1.40 | 46.69 | 0.49 | 0.14 | 0.17 | 0.17 | 0.05 | 0.25 | 37.15 |
| Limestone Asment 2 | 5.84 | 1.94 | 0.87 | 47.79 | 1.17 | 0.20 | 0.42 | 0.10 | 0.03 | 0.03 | 41.33 |
| Shale Asment | 52.07 | 20.10 | 7.32 | 6.41 | 1.08 | 0.07 | 3.33 | 0.97 | 0.11 | 0.15 | 8.15 |
| Pyrrhotine ash | 10.52 | 4.52 | 72.00 | 0.75 | 1.58 | 0.00 | 0.00 | | | | 7.30 |
| Oil shale ash (900°C) | 35.79 | 9.02 | 3.50 | 39.75 | 4.95 | 2.47 | 1.47 | 0.46 | 0.02 | 1.85 | 0 |

The chemical compositions of three clinkers are given in Table 4, which shows that the two developed clinkers contents (clinker (2) and (3)) in major oxide (SiO₂, CaO, Al₂O₃ and Fe₂O₃) are analogous to that of CIMPOR clinker (clinker (1)). However, the clinker (2) content on free lime (3.13%) is higher than the two other clinkers which may be due to the burning conditions (it should be in order of 2% according to 10.1.004-2003 standard) which is an essential parameter for the quality control.

The analysis also showed good combustion of the clinker (3) with respect to prepared clinker (2). This is may be due to the catalytic effect of the minor elements in oil shales.

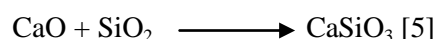
Table 4: Chemical compositions of the three clinkers

| Oxydes | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | TiO ₂ | MnO | P ₂ O ₅ | %CaO free | LOI |
|-------------|------------------|--------------------------------|--------------------------------|-------|------|-----------------|------------------|------------------|------|-------------------------------|-----------|------|
| Clinker (1) | 20.39 | 5.24 | 3.46 | 65.43 | 1.44 | 1.96 | 0.93 | 0.34 | 0.07 | 0.25 | 1.1 | 0.16 |
| Clinker (2) | 21.69 | 5.87 | 3.74 | 65.81 | 1.46 | 0.10 | 0.12 | 0.37 | 0.08 | 0.27 | 3.13 | 0.15 |
| Clinker (3) | 21.33 | 5.54 | 3.81 | 65.60 | 2.01 | 0.25 | 0.10 | 0.34 | 0.06 | 0.43 | 1.23 | 0.1 |

3.2. Chemical Analysis X-ray diffraction (XRD)

3.2.1. X-ray diffraction analysis of Timahdit oil shales

X-ray diffraction analysis of Timahdit oil shales at ambient temperature (Fig.1) revealed the presence of calcite, quartz and dolomite, while the same material calcined at 900°C (Fig.2), showed the existence of quartz (SiO₂), anhydrite (CaSO₄), gehlenite (Ca₂Al (Al-Si) O₇), periclase (MgO) with the formation of wollastonite (CaSiO₃). The later phase was formed from 850°C as a result of the reaction between CaO and silica:



3.2.2. Rays diffraction of the different clinkers

The three diffractograms of the prepared clinkers were established and recorded below (Fig.3).

The XRD patterns of the three clinkers (Fig.3) showed the existence of peaks characteristic of alite (C₃S), belite (C₂S), also the peak of (C₃A) and that of C₄AF. We observed some difference between the patterns (the appearance of new lines and disappearance of others, the increasing and decreasing in peak intensities). These

variations were may be due to the conditions of the preparation of these clinkers and their quenching process from the oven (cement kiln or oven in the laboratory).

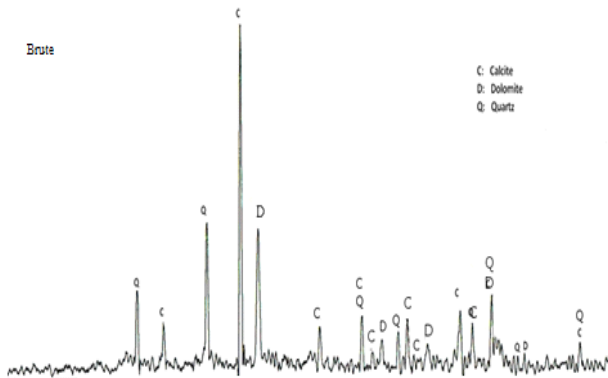


Figure 1: X RD spectra of raw oil shale

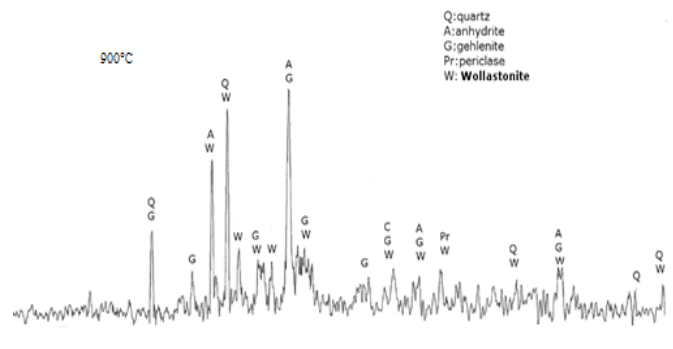


Figure 2: X RD spectra of oil shale burned at 900°C

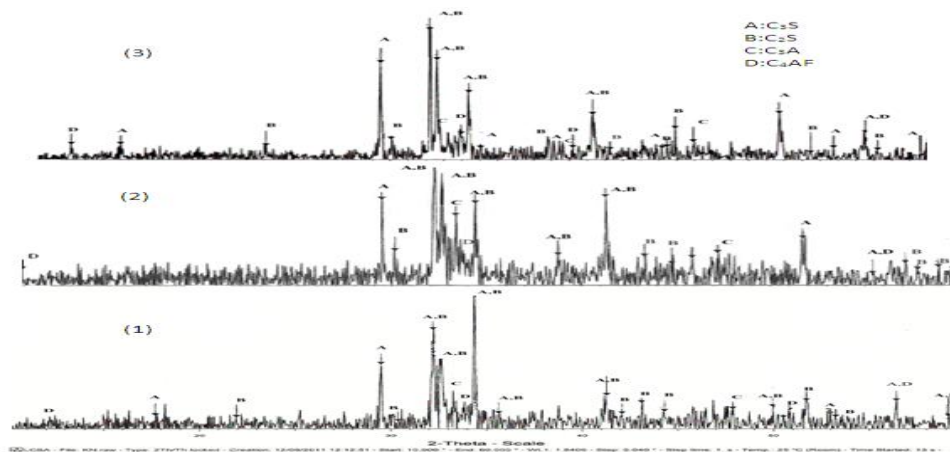


Figure 3: X ray diffraction spectras of three clinkers 1, 2 and 3

The cooling of the clinker has an important role which is the stabilization of certain phases. It was reported that a slow cooling of the clinker decomposed the alite to give belite: $C_3S \rightarrow C_2S + CaO$ [6]. The mineralogical compositions of various clinkers were calculated by the Bogue formulas using the values of oxides in Table 4.

Table 5: Mineralogical composition of clinkers according to Bogue Formulas

| Phases | Content % | | | | % LSF |
|-----------------------------|------------------|------------------|------------------|-------------------|--------|
| | C ₃ S | C ₂ S | C ₃ A | C ₄ AF | |
| Clinker (1) | 56.69 | 8.88 | 8.04 | 10.52 | 99.6 |
| Clinker (2) | 58.06 | 18.36 | 9.24 | 11.37 | 94.30 |
| Clinker (3) | 61.51 | 14.74 | 8.24 | 11.61 | 95.77 |
| Normal Portland clinker [7] | 40-70 | 20-30 | 5-12 | 0-15 | 85-100 |

The results of Bogue formulas showed that the percentages of the four main phases of the clinkers. The result showed that the content of these phases of clinker (2) developed in the laboratory with the same raw materials than those of Asment plant were very close to those of ordinary Portland clinker. However, for the clinker (1), the percentage of belite was very low compared to the clinker (2). This was due to the increase in lime saturation factor (LSF, table 5) which had lead to the reduction of belite content and to the increase of alite [8-9].

3.2.3. Hydration of the clinker 3

The XRD pattern of the clinker (3) has been registered at three days of hydration (Fig.4). The obtained results show the presence of different phases: C₄AF, C₃S, C₂S, CSH, CaCO₃ and Ca(OH)₂. Also the XRD allowed us to

observe the presence of hydrated C_4AH_{13} C_3AH_6 phases (products of C_3A hydration in the absence of gypsum) and the existence of peak characteristic of calcite. The calcite was due to the presence of limestone filler introduced into the clinker as a primary component during its preparation.

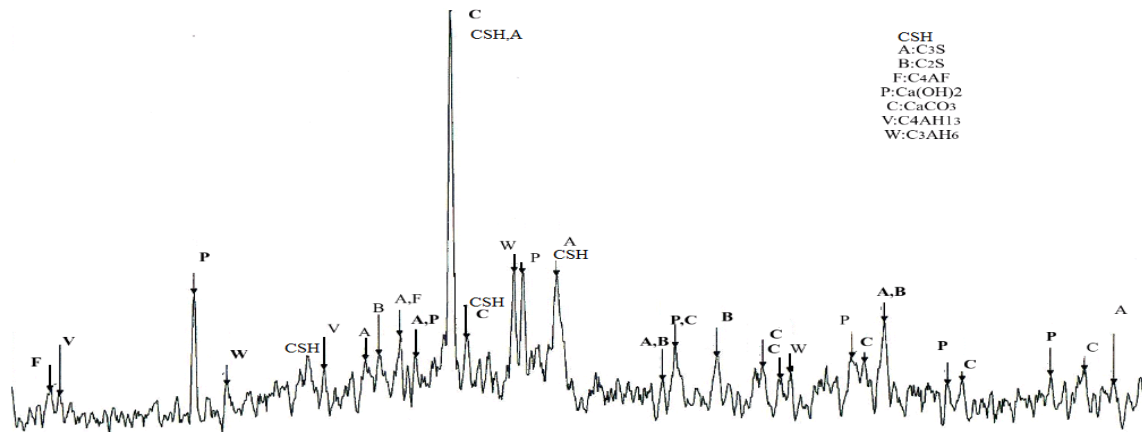


Figure 4: XRD spectra of the clinker (3) hydrated for three days

3.3. Differential Scanning Calorimeter

The differential analysis of the clinker (3) after three days of hydration showed the presence of two endothermic peaks which occur at different intervals. The first broad peak between 22 and 200°C was due to the release of water from the pores and to the decomposition of hydrates. The water released corresponded to the evaporation of water from the humidity of the air and to the material intrinsic water such as the free water and the hydrates bounded water.

The very intense endothermic second peak between 400 and 600°C, corresponds to the dehydroxylation of $Ca(OH)_2$ according to the reaction: $Ca(OH)_2 \longrightarrow CaO + H_2O$ [10]

The dehydration process of the $Ca(OH)_2$ depends strongly on the heating rate [10], however, most researchers associated this phenomenon at temperatures between 400 and 600°C.

Beyond 600°C, we observed the beginning of an endothermic third peak. It corresponded to the decarbonisation of $CaCO_3$ (calcite). The mass loss corresponding to the decomposition of calcite is due to the departure of CO_2 .

The equation of the reaction is as follows: $CaCO_3(g) \longrightarrow CaO(g) + CO_2$ [10]

Calcium carbonate is present in the paste because of the carbonation of free lime present in the clinker

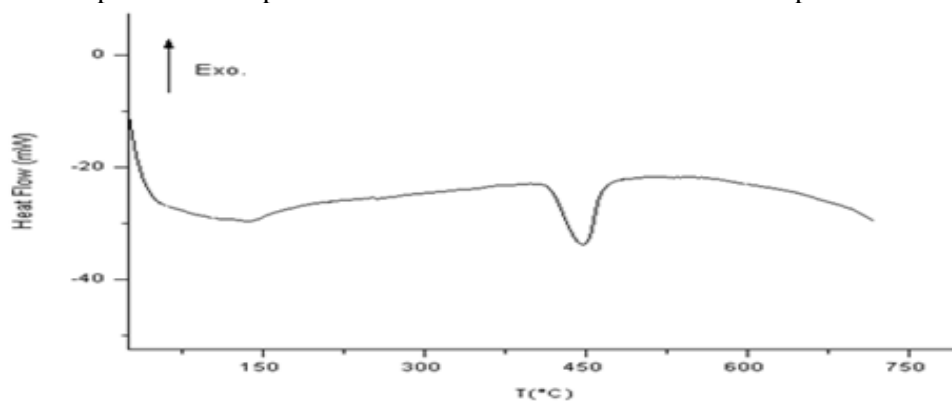


Figure 5: Differential scanning calorimetry of 3 days hydrated clinker (3)

3.4. Scanning electron microscope analysis (SEM)

The oil shale particles burned at 900°C and hydrated for half an hour, as seen by the scanning electron microscope at different magnification (Figure 6) had angular shapes and rough and porous surfaces.

We also observed the existence of quartz grains with no crystal form. These grains vary in size. They are often larger than 30 microns and the smallest are of few microns and they are rounded or irregular.

The analysis by EDAX indicated that the greater number of sample phases contains silica (Si), oxygen (O), calcium (Ca), aluminum (Al), magnesium traces (Mg), phosphate (P), sulfur (S), potassium (K) and iron (Fe). The nature of the peak intensities corresponding to each element may help to identify the phases that exist in the Timahdit oil shale.

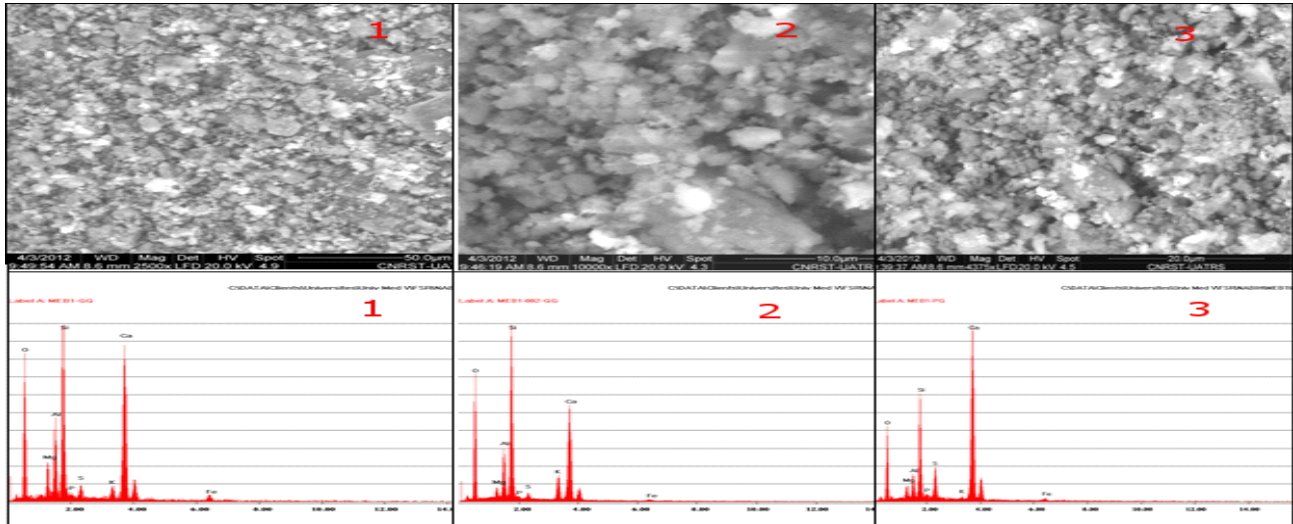


Figure 6: SEM and EDAX oil shale calcined at 900°C then hydrated for half an hour

Table 6: Major and minor elements existing in calcined and hydrated shale samples

| | |
|----------------|----------------------|
| Major elements | Si, O, Al. |
| Minor elements | Fe, Ca, Mg, Na, C, K |

3.5. The effect of oil shale ash on the compressive and flexural strengths

In a previous research, we have studied the effect of the addition of oil shale ash on the mechanical proprieties of mortar using different percentages of oil shale ash as additive to CPJ₄₅. We found that the 28 days compressive and bending strengths of mortar had their maximum values with 10% of OSA with 42.7 Mpa for compressive strength and 7.3 MPa for bending strength [11].

Conclusion

The objective of this research was to study the possibility of using the Timahdit oil shale (sub-layer M) as substitutes to the raw material and evaluating the effects of their ash (calcined at 900°C) on the physicochemical properties of clinker. Based on the results and discussion above, it was found that there is a potential in using the oil shale ash as additives in raw materials to produce the clinker.

XRD identified that the major phases present in the raw oil shale were calcite, quartz and dolomite. Additionally, the 900°C oil shale ash was also examined and showed the presence of quartz, gehlenite, anhydrite, wollastonite, periclase and akermanite. For the prepared clinkers, the analysis revealed that the crystalline phases were those of an ordinary clinker (C₃S, C₂S, C₃A and C₄AF) and the main crystalline phases of the three days hydrated clinker (3) were C₃S, C₂S, C₄AF, C-S-H, calcite, portlandite, C₄AH₁₃ and C₃AH₄.

The study of early hydration of clinker 3 (3 days) by DSC showed the endothermic behaviour of decomposition of carbonate, hydrates and dehydroxylation of Ca(OH)₂.

The results obtained by SEM/EDAX showed that the morphology of the particles that exist in the oil shale calcined at 900°C and hydrated for half an hour are composed of angular shapes, rough and porous surfaces.

The result showed that the composition of Timahdit oil shale ash (OSA) present excellent hydraulic and pozzolanic activities. The use of OSA as additive in the raw materials is a very promising matter, because their use in the raw material gave low value of free lime and higher values of C₃S and β-C₂S (These two phases are responsible of the compressive strength at short and long term respectively) comparing to the clinker (2) prepared with the same experimental protocol without OSA.

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