



Characterization and hydration of cements and pastes obtained from raw mix containing Moroccan oil shale and coal waste as a raw material

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HIGHLIGHTS

- Oil shale and coal waste can be used as alternative raw materials in Portland cement.
- The four hydration steps were observed in all cements containing oil shale and coal waste.
- The cement paste containing oil shale blended with coal waste had the highest compressive strength.

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ABSTRACT

In the present work, the hydration and physical properties of cements obtained from a raw mixes containing oil shale and coal waste as an alternative raw material were explored.

A study of clinkers was carried out using chemical analysis and the hydrated products were characterized by conduction calorimetry, X-ray diffraction, FTIR, Differential thermal analysis-thermal gravimetry and Scanning electron microscope. The findings showed that the cement paste containing both oil shale and coal waste had the highest compressive strength.

According to the hydration studies, the four hydration steps were observed in all cements. The conduction calorimetry study showed the formation of the calcium monosulfoaluminate phase (AFm) in all cements which in cement containing coal waste was retarded by 50 h due to the high Na₂O concentration in its clinker. Further, the identified hydration products: C-S-H gel, portlandite and Afm phase, which detected by XRD, FTIR and ATD/TG have been observed morphologically in SEM images. Moreover, the EDX microstructural study revealed that C-S-H gel contains a less amount of Aluminum and sulfur.

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1. Introduction

A recent study [1] have indicated that the chemical and the mineralogical of Moroccan oil shale and coal waste would make it appropriate for possible use as an alternative raw material for Portland clinker. Oil shale is considered one of the largest energy resources in the world [2]. Morocco has one of the world's largest oil shale reserves [3]. It may be defined as natural rocks consisting of organic and inorganic materials. Timahdit oil shale is known by its four lithological zones (T, Y, X and M). On the other hand, coal wastes are the low-energy-value discards of the coal mining indus-

try in Jerada city [4–6]. The literature shows that oil shale fly ash or coal waste can be used as concrete, cement, bricks, ceramic and other applications [5,7–9].

Furthermore, Portland clinker is made by heating a homogeneous mixture of raw materials in a rotary kiln at about 1450–1500 °C, this high temperature required large energy consumption. Therefore, the valorization of these materials is a great way to reduce the high energy consumption, to reduce also the stockpiling and solving urban planning problems at the same time. On the other hand, the use of alternatives fuels, secondary cementitious materials (SCMs), often industrial by-products, improvements in combustion, heat exchange and grinding technologies along with grinding additives, have diminished both emissions and consumption with no detriment to binder properties [10–13].

The findings [1] have shown that the four layers contain mainly calcite, quartz and dolomite as crystalline phases while a high

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Table 1
Chemical analysis (wt %) of raw materials.

Oxide	CaO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	SO ₃	MgO	K ₂ O	MnO	P ₂ O ₅	LOI
BOS	19.37	8.52	23.94	2.56	3.59	2.1	1.06	0.01	0.25	37.67
CW	0.57	21.63	52.03	4.65	0.91	0.99	2.97	0.06	0.07	14.26

Table 2
Raw mixes proportions (wt%).

	Limestone	BOS	CW	Fe ₂ O ₃
RM-BOS	66	33	–	1
RM-CW	83.06	–	15.54	1.4
RM-BOS + CW	64.71	20.44	13.71	1.14

proportion of quartz (about 65.5%) detected in the coal waste. The both material contain a part of organic matter which allowed us to reduce the clinkerization temperature.

The present paper, carry out the hydration and physical–mechanical behavior of three types of cements prepared from clinkers containing different prime materials (oil shale, coal waste and the mixture of the both) with particle size less than 45 μm.

2. Raw mix, clinker and cement preparation

The materials used in this study were collected from the four lithological zones (T, Y, X and M) of Timahdit oil shale and the coal waste (CW) stockpiled at Jerada. The four layers of Timahdit oil shale were mixed in order to obtain a homogenous blended oil shale (BOS). The BOS and CW were sieved to a particle sizes under 45 μm. The mean chemical composition for BOS and CW, found by X-ray fluorescence (XRF) spectrometry, is given in Table 1.

In order to prepare three different raw mixes, limestone (ground to under 125 μm) was added to the BOS and CW as well as to the both materials BOS + CW (BOS: 20.44% and CW: 13.71%). Ferric oxide (96% pure) was used to correct the iron content.

The raw materials were pelletised, set into platinum crucibles, clinkerised at 1400 °C for 30 min in a laboratory furnace, the clinkers obtained were cooled at ambient temperature, ground and then sieved to under 45 μm.

The percentage composition of the raw mixes is shown in Table 2. Table 3 provides the chemical analysis of clinkers obtained and their results by Rietveld quantitative XRD mineralogical analysis on the clinkers are given in Table 4.

Cements were obtained by mixing clinkers obtained with pure gypsum (Ca₂SO₄, 2H₂O) in proportions that would ensure that the SO₃ content in the final cement would not exceed 3%. The clinker and gypsum were blended in a turbula for 24 h.

3. Hydration analytical techniques

Hydration was followed by conduction calorimetry; about 3 g of these anhydrous cements were mixed with distilled water at the water/solids ratio 0.4. After mixing with a spatula for 3 min, the 120 h calorimetry trial was conducted at a constant temperature of 25 °C.

Table 3
Chemical analysis of elaborated clinkers, expressed in oxides (wt%).

Oxide	CaO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	SO ₃	MgO	K ₂ O	Na ₂ O	ZnO	P ₂ O ₅
Clk-BOS	62.43	7.1	18.69	4.25	1.58	2.15	0.72	0.05	0.03	0.58
Clk-CW	62.41	7.95	20.38	4.14	0.06	0.97	1.02	0.14	0.01	0.05
Clk-BOS + CW	63.22	7.04	18.61	4.12	1.42	1.87	0.87	0.07	0.02	0.44

Table 4
Quantitative analysis of the mineralogical phases in clinkers (wt%).

Phase	Clk-BOS	Clk-CW	Clk-BOS + CW
C ₃ S (Ca ₃ SiO ₅)	70	56.4	74
C ₂ S (Ca ₂ SiO ₄)	10.23	28.17	10.3
C ₃ A (Ca ₃ Al ₂ O ₆)	3.5	8.5	4.53
C ₄ AF (Ca ₄ Al ₂ Fe ₂ O ₁₀)	11.72	6.52	11.52

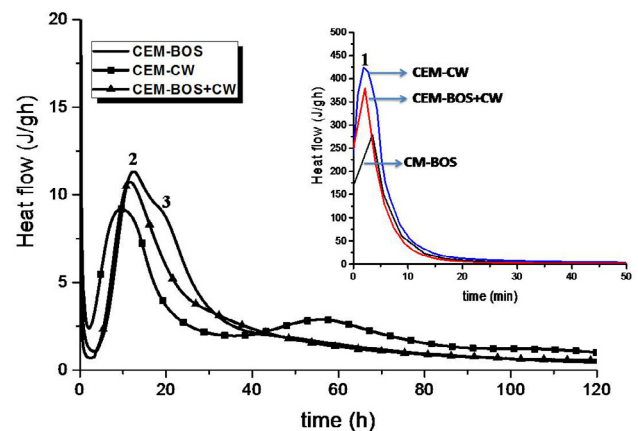


Fig. 1. Conduction calorimetry curves showing the heat flow evolution in the CEM-BOS, CEM-CW and CEM-BOS + CW pastes.

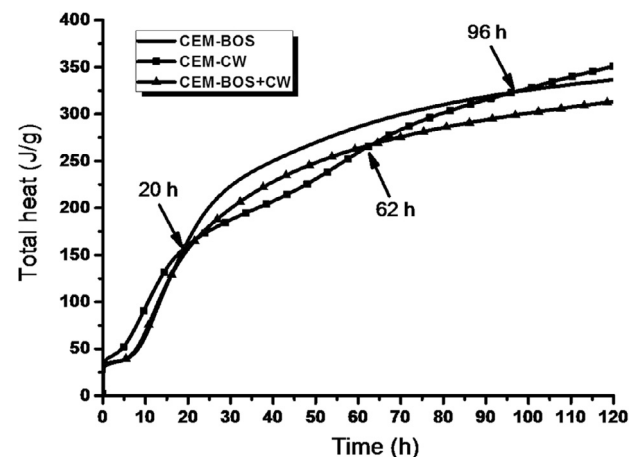


Fig. 2. Conduction calorimetry curves showing the total heat evolution in the CEM-BOS, CEM-CW and CEM-BOS + CW pastes.

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