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Valorization of industrial waste as a cement addition

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Abstract
The objective of this work is to valorize the fly ash and oil shale ash in cement manufacturing. The use of the two products was preceded by a characterization by X-ray diffraction, and X-ray fluorescence. The addition was made to several percentages (5 %, 7 %, 10 %, 15 %, 20 %) affine to determine the best percentage of addition. The cements which have shown a good mechanical resistance were analyzed by Differential Scanning Calorimetry (DSC) before and after 3 days of hydration.
The results obtained from this research show that fly ash is rich in silica and alumina, and it consists principally of mullite, hémalite, magnetite, and quartz. By against calcined oil shale are rich in CaO and are composed of quartz, calcite, anhydrite, periclase and wollastonite. The results of the mechanical resistance showed that the best percentage of addition for the fly ash is 7 % and the calcined oil shale is 10 %. The study of hydration to 3 days has allowed levying the dehydration peaks of $CaO.2SiO_2.3H_2O$ and $Ca(OH)_2$.

1. Introduction

Every cement industry aims to optimize production, improve performance, protect the environment and preserve natural resources [1-3]. The use of industrial by-products in the cement manufacture not only improves the thermal balance in an energy-intensive sector, but also provides a solution to the problems of environmental pollution related to storage in the heaps form, or the dumping of industrial by-products at sea [4].

Fly ash (FA) and from oil shale ashes (OSA) are among the by-products of thermal power plants that contribute to the development of cement performance. Several authors have studied the effect of FAs on the cement properties [5-7]. El Khadiri has shown that the addition of fly ash contributes to the increase of the cement mechanical resistance [8]. Morocco's tar shales(Tarfaya)

were studied by Bekri and Nabih who studied the effect of adding OSAs to cement and found that they improve the cement mechanical properties [9, 10].
The present work is a mechanical behavior study of new families of cements prepared by adding different percentages of the FAs and OSAs of the Timehdit region.

2. Expérimental details

2.1. Materials

The raw material used for the preparation of the cements was supplied by the Asment factory (Votorantim Cimentos) in Ain Atiq. The clinker is taken directly from the cooler. Gypsum and secondary limestone are extracted respectively from quarries operated by the plant at Aian Atiq and Khmissat.

The FAs used were provided by the Jorf Lasfer Thermal Power Plant. The oil shale of the Timehdit region was supplied by the ONHYM (National Office for Hydrocarbons and Mines). The latter were calcined in a laboratory oven at 900 °C for 1 hour, to remove the organic fraction and obtain ashes (OSA).

2.2. Methods

2.2.1. Cements preparation

The tests were carried out on the class of Composite Portland Cements CPJ_{45}. The cement components (75 % clinker, 21 % limestone, 4 % gypsum) were milled using a ball mill. The grain size of the cement was monitored during grinding in order to eliminate its impact on the mechanical properties. Monitoring was performed using the sifter to set the refusal 80 µm at 2% ± 0.1.

The sum of FAs and OSAs was calculated according to the following equations:

- $CPJ_{45\ X\ FA} = (100 - X)\ \%\ CPJ_{45} + X\ \%\ FA$
- $CPJ_{45XOSA} = (100 - X)\ \%\ CPJ_{45} + X\ \%\ OSA$

With: X = 5, 7, 10, 15, 20

2.2.2. Mortars preparation

For the realization of the mechanical tests, the normal mortar was prepared according to the Moroccan norm 10.1.005 [11], respecting the following proportions:

- 1350 g of normal sand,
- 450 g of the cement,
- 225 g of water.

The ratio Water / Cement is the order of 0.5.

The prepared mortars were introduced into 4 * 4 * 16 cm prismatic molds for storage in a wet cabinet. After 24 hours, the test pieces were demolded and kept in water at 20 °C until the day of the test (2, 7 and 28 days).

The mortar bending strength was determined by three-point loading until the cured mortar sample broke. The compressive strength of the mortar was determined on the two half specimens resulting from the bending strength test.

2.2.3. Characterization methods

- The elemental analysis of all cement components was made by Fluorescence X, by using a PAN analytical spectrometer PW 4400/24.

The crystallographic study was carried out for the powdered FA and OSA samples by a Siemens D5000 diffractometer. The device uses the BRAGG - BRENTANO circuit and a radiation $\lambda_{K\alpha Cu}$ = 1.5406 Å. The range of the spectra is between 10 and 60 ° with a pitch of 0.04.

- To determine the variation of thermal flux emitted or received by the cement subjected to a temperature gradient and to detect the transformations accompanying the heat exchange, we carried out a thermal analysis by Differential Scanning Calorimetry (DSC) for the cements prepared with using a DSC 121 calorimeter from the SETARAM company.

The analyzes were carried out under pure argon scavenging, using a platinum crucible to avoid any reaction of the samples with the atmosphere of the furnace and the material constituting the crucible. The temperature range was between ambient and 750 °C. The heating rate is set at 10 °C per minute.

The study was carried out on anhydrous and hydrated samples at 3 days (Water / Cement = 0.5) for the cements showing the best mechanical behavior at 28 days.

3. Results and discussion

3.1. Characterization

3.1.2. X-ray fluorescence

The results of X-ray fluorescence analysis of the products used and reduced to powder, are presented in weight percentage at Table 1.

Elements	***SiO_2***	***Al_2O_3***	***Fe_2O_3***	***CaO***	***MgO***	***SO_3***	***K_2O***	***TiO_2***	***MnO***	***P_2O_5***	***Na_2O***
Clinker	20,73	5,19	3,55	64,62	1,63	2,02	0,86	0,36	0,08	0,35	0,18
Limestone	14,73	1,34	1,67	46,31	0,51	0,11	0,17	0,21	0,05	0,33	0,07
Gypsum	-	-	-	-	-	41,14	-	-	-	-	-
FA	50,76	23,05	4,80	3,23	1,25	0	2	1,13	0,03	0,43	0,12
OSA	34,84	8,93	3,7	41,89	4,97	1,02	1,61	0,47	0,02	1,77	0,48

Table 1: Chemical composition of the products used

The chemical composition of the FAs reveals a high content of silica (SiO_2) and alumina (Al_2O_3) and a low content of CaO. CVs are then classified as Class F silicoaluminous ash with pozzolanic properties.

CSBs can be classified as Class C sulphocalcic ash, and thus have a hydraulic character due mainly to the high CaO content. It should be noted that the high level of MgO and P_2O_5 may have negative effects on the cement.

The mineralogical composition of clinker (Table 2) is determined from the chemical composition, using the following Bug formulas [12]:

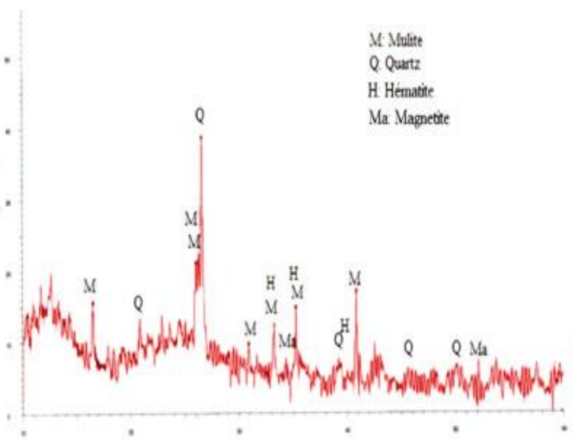
- Alite: C_3S = 4.071 CaO - 7, 60 SiO_2 - 6,718 Al_2O_3 - 1,430 Fe_2O_3
- Belite: C_2S = 8.602 SiO_2 - 5.068 Al_2O_3 - 3.071 CaO + 1.078 Fe_2O_3
- Aluminates: C_3A = 2,650 Al_2O_3 - 1,692 Fe_2O_3
- Ferrite: C_4AF = 3.043. Fe_2O_3

Mineralogical composition of clinker	**C_3S**	**C_2S**	**C_4A**	**C_4AF**
Percentage	59,76	14,34	7,76	10,81

Table 2: Mineralogical composition of clinker

3.1.2. X-ray diffraction

The X-ray diffractogram (XRD) of FAs (Figure 1) shows the presence of three crystalline phases: quartz, mullite, magnetite and hematite. The halo located between 2θ = 20 ° and 2θ = 30 ° proves the existence of a vitreous phase. For OSA (Figure 2), the major crystalline phases are: quartz, gehlenite, calcite, anhydrite, wollastonite and periclase.



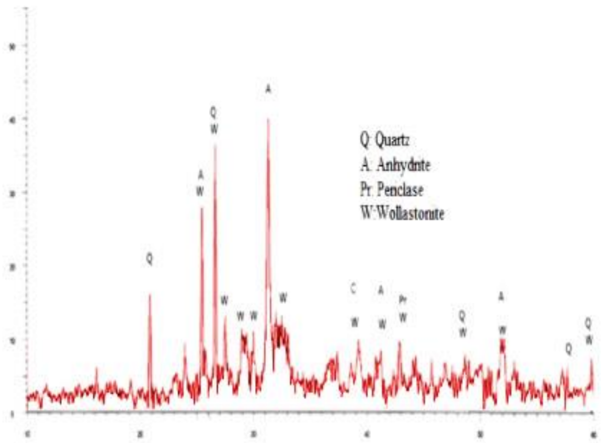


Figure 1: X-ray diffractogram of FAs Figure 2: X-ray diffractogram of OSAs

3.2. Mechanical resistances

The results of the mechanical tests are shown in Figures 3 and 4. For all the families of the elaborated cements, a continuous increase of compressive strength and bending with time has been marked. This is due to the hydration phenomenon of the cement which causes the compactness evolution with the time. Indeed, the hydration of C_3S and C_2S cement constituents, according to the reactions below, gives rise to the formation of $CaO.2SiO_2.3H_2O$ hydrated calcium silicates (CSH), which contribute to the increase of mechanical strengths according to the following reactions [13]:

$$\mathbf{2\ (3\ CaO.SiO_2) + 6\ H_2O \rightarrow 3\ CaO.2SiO_2.3H_2O + 3\ Ca(OH)_2} \quad \mathbf{(1)}$$

$$\mathbf{2\ (2\ CaO.SiO_2) + 4\ H_2O \rightarrow 3\ CaO.2SiO_2.3H_2O + Ca(OH)_2} \quad \mathbf{(2)}$$

In addition, the mechanical resistance at 28 days decreases to 5 %, and increases to 7 % for the FA cements family, with a difference of 1.7 MPa in compression and 0.1 MPa in flexion compared to the control cement.

Above 7 %, the mechanical strengths decrease. The same results were obtained by the similar study conducted by El Khadiri and Quaboul [8, 14]

For OSA cements families, the resistances at 28 days increase gradually after 5 % addition and reach the maximum at 10 %, with a difference of 3.3 MPa in compression and 0.2 MPa in flexion compared to cement witness. This result corroborates that of Al Hamaniedh and All [15] who made a similar study with Jordan's oil shale. In addition, the CPJ_{45} cement families with 15 % and 20 % of OSA show a decrease compared to the control. We note that the substitution of CPJ_{45} with 15 % of OSA or FA leads to the same results in terms of mechanical strength.

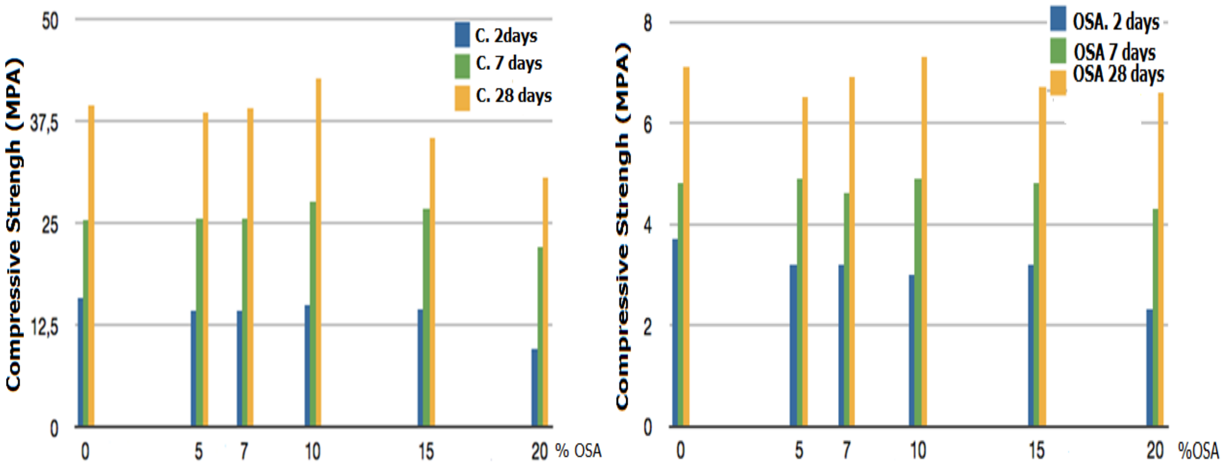


Figure 3: Mechanical strengths of the cement family with OSA addition

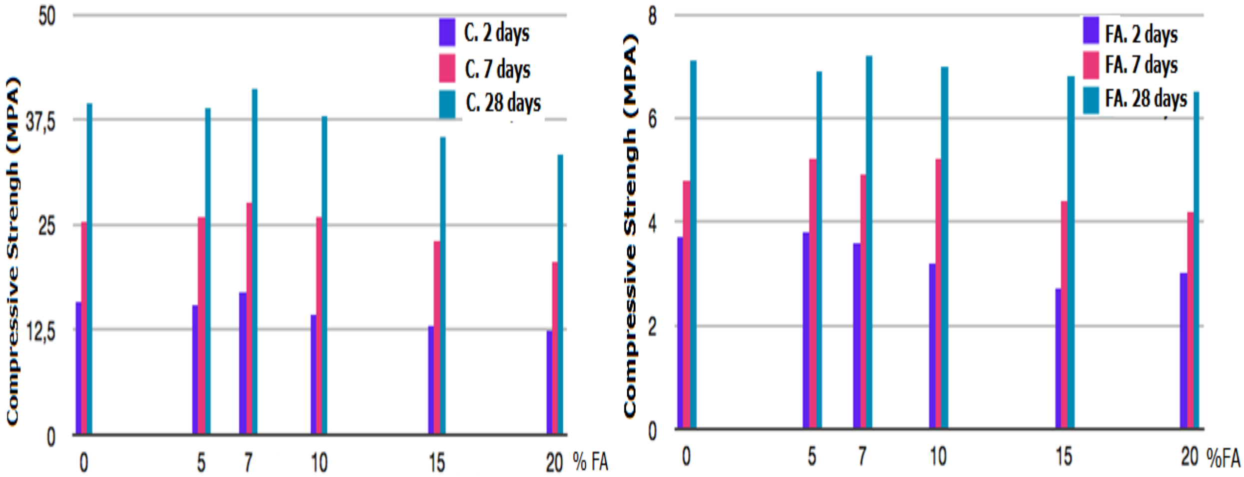


Figure 4: Mechanical strengths of the cement family with FA addition

3.3. Differential Scanning Calorimetry (DSC)

The DSC curves of the $CPJ45_{7FA}$ hydrated and $CPJ45_{10OSA}$ families of cements, shown in Figure 5, have three endothermic peaks.

The first peak between 100 and 150 °C is due to the dehydration of CSH. The shoulder to the left of the first peak reflects the loss of free water. It should be noted that $CPJ45_{10OSA}$ cement dehydrates at a slightly higher temperature than $CPJ45_{7FA}$ cement.

The second peak recorded between 400 and 500 °C corresponds to the dehydration of portlanditeCa $(OH)_2$ according to the following reaction:

$$Ca(OH)_2 \longrightarrow CaO + H_2O_{(g)} \qquad (3)$$

From 600 °C, the heat flow decreases giving a third peak, which corresponds to the departure of CO_2 from the decomposition of calcite according to the following reaction: $CPJ45_{7FA}$

$$CaCO_3 \longrightarrow CaO + CO_{2(g)} \qquad (4)$$

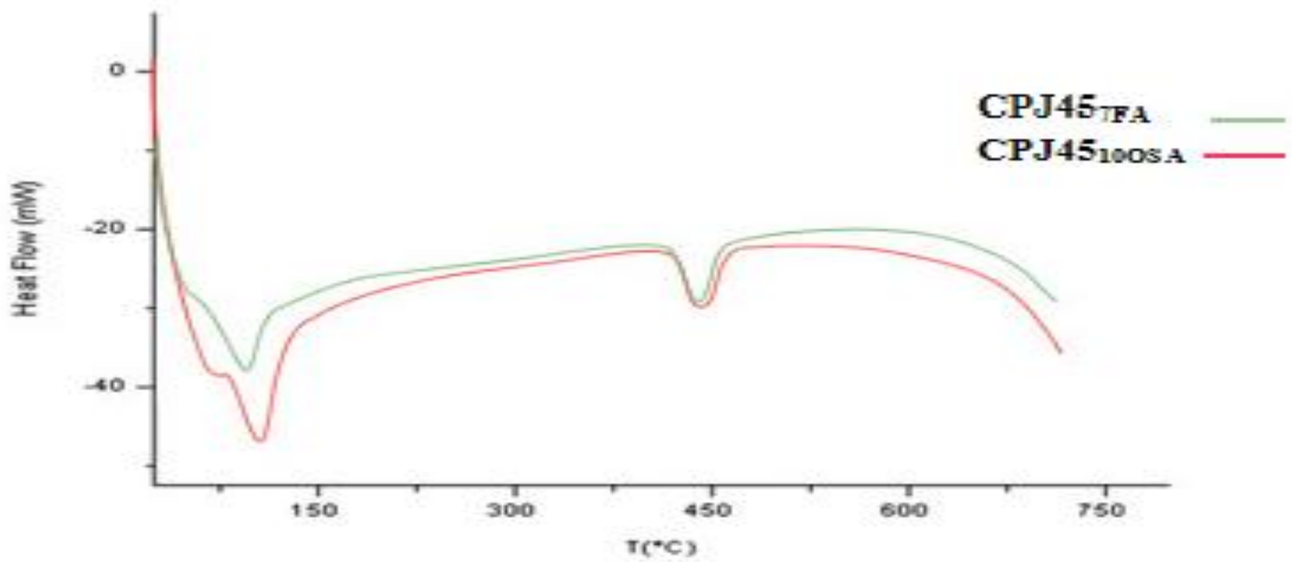


Figure 5: DSC Curve of $CPJ45_{7FA}$ Hydrated and $CPJ45_{10OSA}$ Cement Families

The DSC curve of the anhydrous $CPJ45_{7FA}$ and $CPJ45_{10OSA}$ cements families' shows (Figure 6) three endothermic peaks. The first peak between 100 and 150 °C, with a maximum at 110 °C may be related to the dehydration of the absorbed water, or the decomposition of the gypsum used to prepare the cements.

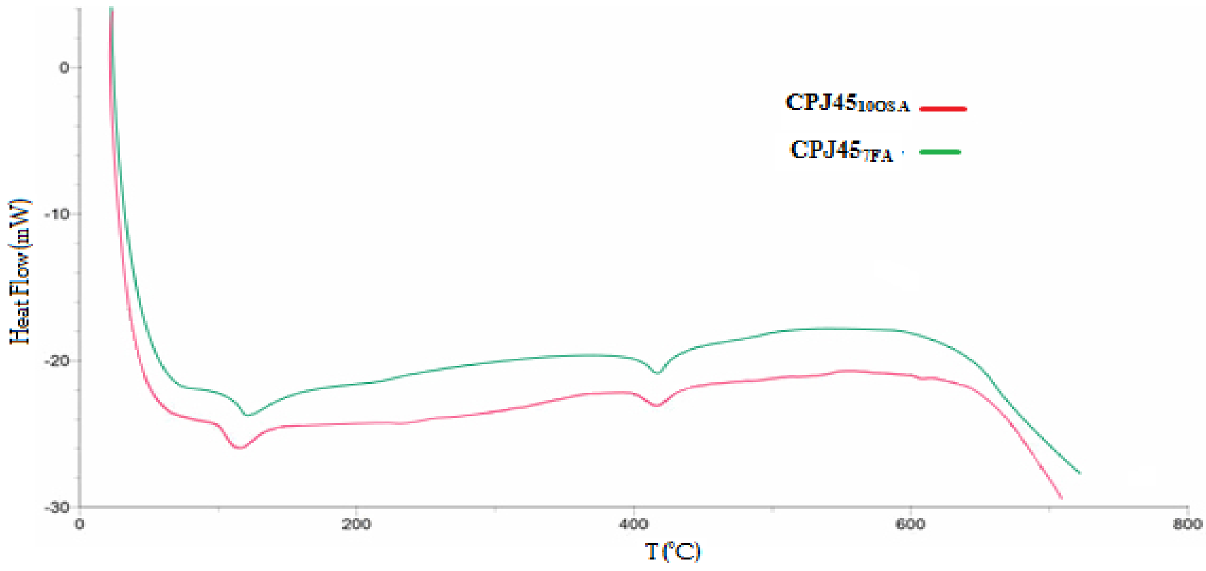


Figure 6: DSC Curve of $CPJ45_{7FA}$ and $CPJ45_{10OSA}$ Anhydrous Cement Families

The second peak of lower intensity can be interpreted as a dehydration of $Ca(OH)_2$ formed in contact with the humidity of the ambient air, in spite of the precautions taken for the cements conservation. The third peak above 600 °C reflects the calcite decomposition from limestone added during clinker grinding.

Conclusion

The present work aiming at the valorization of FAs and OSAs in the cement manufacture makes it possible to draw the following conclusions:

- FAs belong to class F, and thus have pozzolanic properties. While the OSAs belong to class C and possess hydraulic properties.
- FAs contain quartz, mullite, hemallite and magnetite. OSAs are composed of quartz, anhydrite, gehlenite, wollastonite and periclase.
- Mechanical strength reaches its maximum at 7% FA, and 10 % OSA.
- The $CPJ45_{7FA}$ and $CPJ45_{10OSA}$hydrated cements families showed endothermic peaks related to the dehydration of CSH, CH and the calcite decarbonation. The same cement families in the anhydrous state showed endothermic peaks related to the dehydration of the absorbed water, the decomposition of hydrates formed in contact with the humidity of the ambient air and the calcite decarbonation.
- The use of industrial by-products in the cements production can solve the problem of their management. It also makes it possible to lower the clinker consumption according to the additions rates, and to obtain cement whose performances are as good as those of a cement of the same class of resistance.

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