Effects of the addition of oil shale ash and coal ash on physic-chemical properties of CPJ$_{45}$ cement

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Abstract. We focused our research on recycling industrial wastes, fly ash (F.A), bottom ash (B.A) and oil shale ash (S.A) in cement production. The study concerns physico-chemical characterization of these products and the influence of their addition on the mechanical proprieties of the CPJ$_{45}$ cement. XRF allowed us to rank the three additives used according to their contents on major oxides. Coal ashes belong to the class F, and thus possess poozzolanic properties and oil shale ash belongs to the class C and possesses hydraulic and poozolanic properties. The crystalline phases constituting each ash were analysed by XRD. We observe in bottom ash the presence of quartz and mullite. The same crystals are found in fly ash with hematite and magnetite. Oil shale ash is composed of quartz, anhydrite, gehlenite, wollastonite and periclase. The microstructures of fly ash and bottom ash were studied using SEM. The bottom ash was composed respectively of fine particles that are generally irregularly shaped, their dimensions are between 5 and 28μm and of big particles(300 μm). The EDX analysis coupled with an electronic microscope provided some information about the major elements that constitute our samples. The dehydrations of anhydrous and three days hydrated cement were examined by DSC. For hydrated cements we noticed endothermic peaks related to the dehydration of CSH, CH and decomposition of carbonates. The study of the mechanical properties of CPJ$_{45}$ cement by adding different proportions of fly ash, bottom ash and oil shale ash helped clarifying the percentage of ash that leaded to improve the 28 days mechanical strength. The results show that the cements studied have their maximum mechanical resistance with the addition at 7% of fly ash or 10% of oil shale ash.

1- Introduction

It is reasonable to believe that for energy saving the use of oil shale ash or coal ash as additive to clinker or cement will continue and grow more. They permit the production of cement with performance as good as Portland cement with the same strength and often with better chemical resistance. The replacement of Portland cement with additives has many advantages: It reduces CO$_2$ emissions, provides a solution to the problems of pollution related to storage in heaps, or ocean dumping of industrial by-products [1]. The cements obtained benefit of greater workability, better water resistance with a reduction of the heat of hydration and the risk of cracking due to thermal action. They have also greater durability to sulfate or acidic medium [2].

Morocco is one of the world leading countries in term of oil shale resources [3]. The oil shale ash is used on an industrial scale for cement production in several countries in the world.

Mining and processing of the oil-shale will significantly disturb the environment, as a result of pollution by dust particles and ash derived from the oil shale [4, 5]. Valorisation of these valuable by products will reduce the environmental impact and will make oil shale development economically feasible for energy production in the future. They are two possibilities of using oil shale in cement production: They are either introduced directly at the kiln following the same circuit as the raw materials or the ash obtained after their combustion in a thermal power plant is used as an additive to the clinker. In Estonia and China the ash obtained after burning shale in power plants are valued as by products in the production of cement [6].In the United States the shale is used to a percentage of 20% in raw materials [7]. In Germany the major part of burnt shale is mixed with clinker at the final grinding at 30% ash and 70% of clinker [8]. In Morocco the studies showed that the compressive strength measured on a sample of 30% of Tarfaya shale ash and 70% cement is acceptable by the

standard corresponding to CPJ$_{35}$ cement [9]. In the light of these data, we have conducted research on the valuation of coal ash (fly and bottom ash) and oil shale ash in the development of CPJ$_{45}$ cement.

2 Materials and methods

Timahdit oil shale has been given by ONHYM (National Office of Hydrocarbons and Mines). It is constituted of 24% of clays, 21% of calcite, 15.9% of dolomite, 19% of quartz 1% of pyrite and 17.7% of kerogen. The deposit of oil shale lies in the chain of the Middle Atlas south-east of Rabat at 35 km south of Azrou [10].

The clinker and raw material used for the preparation of cement was provided by the laboratory of the factory Asment (CIMPOR). Fly ash and bottom ash are produced from the combustion of coal in Jorf Lasfer power plant.

2.1 Preparation of raw materials

Gypsum, limestone, clinker and oil shale have been crushed in a jaw crusher (old generation Fritsh pulverisette, 01-703 kind) to minimize their sizes. Bottom ash and limestone were dried in an oven at 110° for four hours and gypsum at 40°C for two hours.
Fly ash, bottom ash and dried crushed oil shale have been finely ground to achieve 80 microns refusal, using a mixer mill oscillating disc (former SIEBTECHNIK generation). After crushing the oil shale were burned at 900°C for 30 minutes

2.2 Preparation of cement

The cements on which we conducted our study were prepared according to the process of production designed in Moroccan cement. A ball mill was used to grind the components (75% clinker, 21% limestone and 4% gypsum), to obtain the CPJ$_{45}$ cement, then we have proceeded to the substitution of the cement by different percentages of fly ash, oil shale ash or (5%) of bottom ash. The cement was monitored during grinding with a sieve to secure 80 microns refusal, with the aim to eliminate the impact of particle size on the mechanical properties.

2.3 Preparation of test specimens

For the realization of mechanical tests (resistance to bending and compression), samples were prepared from normal mortar composed of: 1350 g normal sand (97% silica), 450g of cement and 225g of water. The water/ cement ratio was about 0.5. The mixture of binder and water was placed in a typical automatic Perrier mixer with automation, electric timer and door security cabinet. The minimum and maximum speeds are respectively of the order of 140tr/min and 280tr/min. After mixing at low speed the binder, sand was introduced. The mixer rotation was accelerated for 60 sec until a homogeneous mortar was obtained. The mold (dimensions 4x4x16cm3) was filled with mortar and maintained in a humidity armoire

for 24h at a temperature of 20°C, and then removed from the mold and stored in water to measure the flexural and compressive strength of the samples after 2,7 and 28 days.

2.4 DSC analysis

The hydration was carried out for the cements studied with the 28 days highest strength. Hydrated paste was made by adding water directly to the cement, the water to cement ratio was equal to 0.5. The paste was mixed manually in a beaker using a spatula until obtaining a homogeneous mixture that was kept at room temperature. The hydrated cement was washed by acetone after 3 days and kept in dry place until analysis.

3. Results and discussions

All the raw materials with clinker, fly ash, bottom ash and oil shale ash used in this study were analyzed by fluorescence X. and X-ray diffraction. Bottom ash was analyzed by infrared spectroscopy, and scanning electron microscopy (SEM) coupled with chemical analysis (EDX). Hydrated cements were analyzed by differential scanning calorimeter (DSC). Chemical analysis was used to determine the percentage of free lime in the clinker.

3.1 X rays fluorescence (XRF) analysis

Table.1 .Chemical composition of the starting materials (weight %)

Oxides	Clinker	lime	Fly ash	S.A	B.A
SiO$_2$	20.73	14.73	50.76	34.84	49.86
Al$_2$O$_3$	5.19	1.34	23.05	8.93	18.23
Fe$_2$O$_3$	3.55	1.67	4.80	3.7	9.07
CaO	64.62	46.31	3.23	41.89	10.91
MgO	1.63	0.51	1.25	4.97	1.43
SO$_3$	2.02	0.11	0	1.02	0.17
K$_2$O	0.86	0.17	2	1.61	1.59
TiO2	0.36	0.21	1.13	0.47	0.96
MnO	0.08	0.05	0.03	0.02	0.09
P$_2$O$_5$	0.35	0.33	0.43	1.77	0.34
Na$_2$O	0.18	0.07	0.12	0.48	0.15

The chemical compositions of fly ash, bottom ash, oil shale ash, clinker and lime are given in Table 1 witch shows that fly ash and bottom ash are rich in SiO_2 and Al_2O_3 and contain small percentages of CaO. These ashes can be classified as silico-aluminous class F ashes with pouzzolanic properties because their percentage of CaO is of the order of 3.23% and the sum of SiO_2, Al_2O_3 and Fe_2O_3 is equal to 78.61% [11].The oil shale ash may be classified as being class C ash with a hydraulic character due to their high CaO content (41.89%) and the sum of SiO_2, Al_2O_3 and Fe_2O_3 is lower than 70% (47.67%)[11]. The lime used in this study is rich on CaO and SiO_2. From the same table 1 we can see that all values of the major oxides (SiO_2, Al_2O_3, Fe_2O_3 and CaO) of the clinker used in this study are within the limits of the composition of ordinary Portland clinker [10]. The mineralogical composition of this clinker is also similar to an ordinary Portland clinker. Gypsum and free lime (CaO %) were also analyzed by of XRF. The results show that the purity of the gypsum is of the order of 88.45% and that of SO_3 is of the order of 41.14% (percentage by weight). Free lime composition measured is equal to 1.064%. A quantity above 2% of free CaO can modify the mechanical properties of the cement, and cause it to swell as passing under $Ca(OH)_2$. In our case we can say that the clinker used will not affect the mechanical properties of the cement, and that its quality meets the requirements of the standard Moroccan.

3.2 X rays diffraction (XRD) analysis

X-ray diffraction analysis was carried out, to determine the crystalline phases present in the samples of fly ash, bottom ash and oil shale ash. For the fly ash (Fig.1) we observe the existence of quartz, mullite, magnetite and hematite. We also note the presence of a halo between $2\theta = 20°$ and $2\theta = 30°$ proving the existence of a glassy phase. For the bottom ash (Fig. 2) we notice a glassy phase that is characterized by a halo between $2\theta = 20°$ and $2\theta = 27°$, we also observe the presence of peaks characteristic of mullite and quartz. This result is consistent with that of Cheriaf and all [12] that had shown by X-ray diffraction the existence of quartz and mullite in the bottom ash they studied. For the oil shale ash we observe (Fig. 3) the presence of quartz, gehlenite, calcite, anhydrite, wollastonite and periclase.
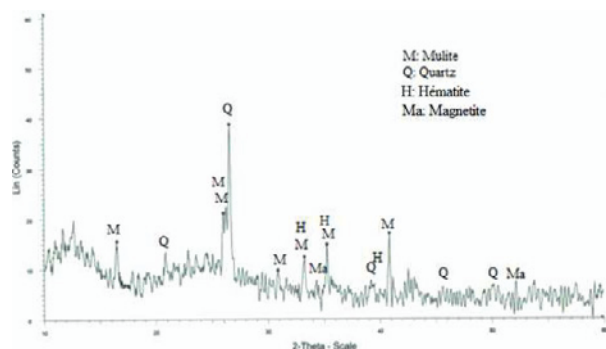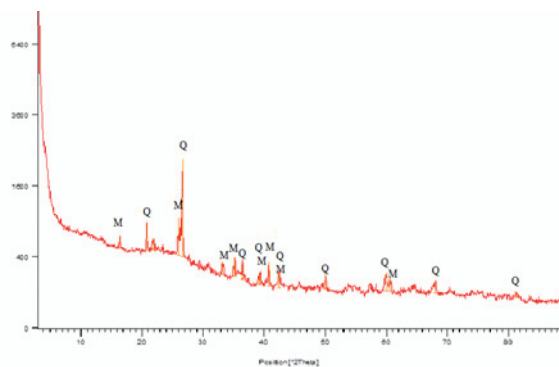

Fig.2 XRD patterns of fly ash
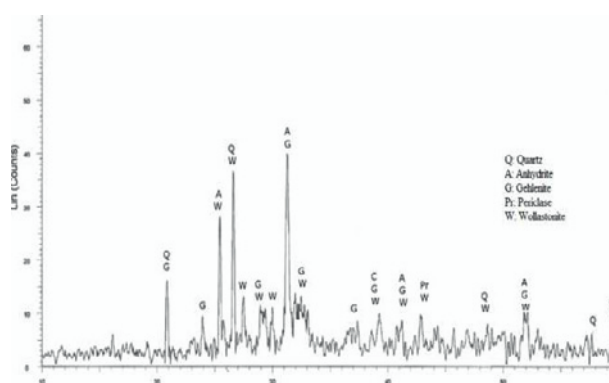

Fig.1. XRD patterns of bottom ash

Fig.3 XRD patterns of oil shale ash

3.3 Scanning electron microscopy (SEM) coupled with chemical analysis (EDX)

Analysis by scanning electron microscopy was performed to determine the morphology and the microstructure of the phases that constitute the sample of fly ash [13] and bottom ash used as an additive to CPJ_{45} cement.

The photographs (Figs.4-6) show the morphology of bottom ash. We note that the sample consists of a fine powder having spherical particles with diameters between 1.5 and 6 μm. We also observe other particles that have irregular shapes with diameters between 5 and 300μm (quartz particle, Fig.6). EDX analysis of the elemental composition of the photographed regions allowed us to found the major and minor elements in our sample (Table 2)

Table 2. Somme elements in the bottom ash

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

3.4 Infrared spectra of Bottom ash

The infrared (IR) analysis result of the bottom ash (Fig 6) shows the presence of bands that characterize the deformation and elongation vibrations of SiO_2 detailed in

Table 3. The wide OH band centered at 3421 cm^{-1} is may be due to the absorption of water during the milling and preparation of the pellet.

The shoulder located at 1423 cm^{-1} is attributed to the vibration CO_3^{2-} group of calcium carbonate which may be due to the carbonation of the samples during their exposure to the atmosphere [14].

The IR analysis result supports the results of XRD and SEM analysis, which confirms the richness of bottom ash on quartz.
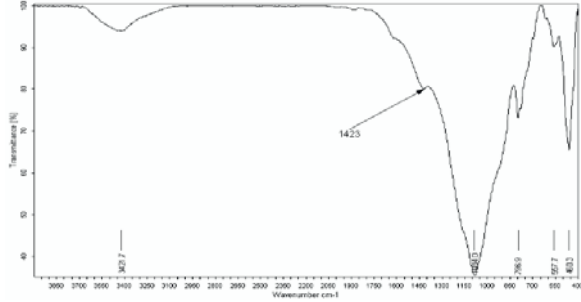

Fig. 6. Infrared spectra of bottom ash

Table 3. Assignment of vibration bands of SiO2

Bands (cm-1)	Assignments
450	Bending vibration in δO-plane
557	Bending vibration in δO-plane *
796,9	Symmetric stretch vibratio O-Si
1094	Stretching vibration vSi-
3421	Bending vibration in the p δO-H *

3.5 Mechanical proprieties

Mechanical proprieties study was carried out on the cements prepared according standard Moroccan NM 10.01.004 cement. We used different percentages of fly ash, bottom ash or oil shale as additive to CPJ$_{45}$.to study their influence on the compressive and the bending strength of the mortars. The results of these mechanical tests are summarized in Table 4. The figures.7 to.9 show the curves of the evolution of compressive strength based on the percentage of fly ash and oil shale ash added. After 28 days of hydration.(fig.10), we observe after a slight decrease of resistance with 5% of fly ash a sudden increase with 7% of the same ash that peaked at 41.1 MPa for the compressive strength and 7.2 MPa for bending strength. Beyond this value we see respectively a gradual decrease of resistances with 20% of fly ash 33.3 MPa and 6.5 MPa for compressive and bending strength.

Nabih et al have studied the influence of the addition with different percentage of fly ash on the mechanical properties of the clinker, and they reported that the compression and bending resistances for these mixtures went through a maximum at 28 days with the addition of 7% (by weight) of fly ash [13,15] Al Hamaniedh and all have studied the compressive strength of a series of cement prepared by addition of Jordan oil shale ash, and they found that the best mechanical resistance to compression is marked for cement prepared with 10% of ash[16]. In our case we observe a slight decrease of resistance with the addition of 5% of oil shale ash, followed by a gradual increase which peaked at 10%, with 42.7 MPa for the compressive strength and 7.3 MPa for the bending one. The mechanical resistance decreases sharply after the addition of 10% of oil shale.
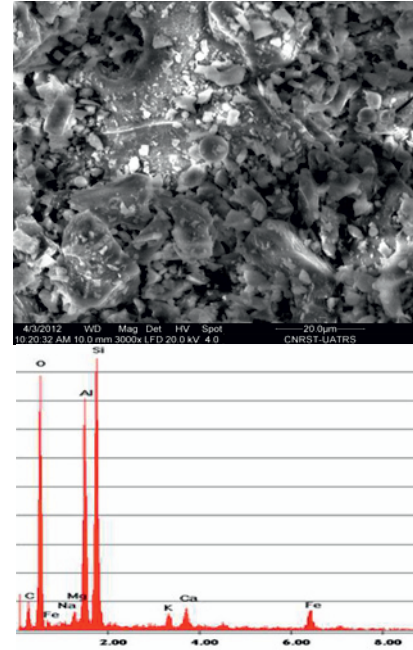

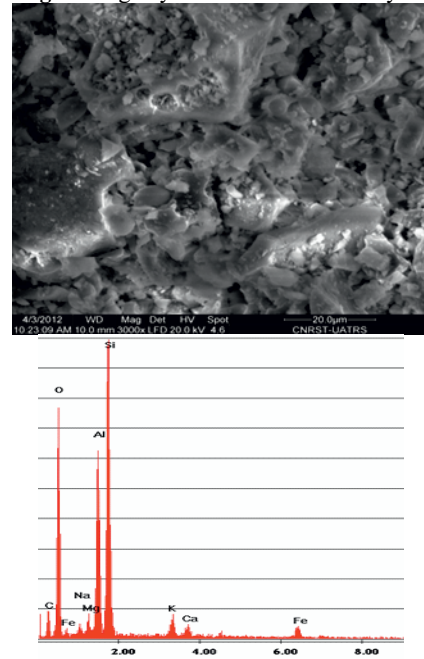**Fig.4**: Image by SEM and EDAX analysis

Fig.5: Image by SEM and EDAX analysis

same percentage of F.A or S.A. This result is in agreement with those of Canpolat et all.[17]. We may confirm that the addition of 5% of B.A greatly improves the mechanical properties of the cement,by 4.7 MPa for compressive strength and 0.7 MPa for bending strength.
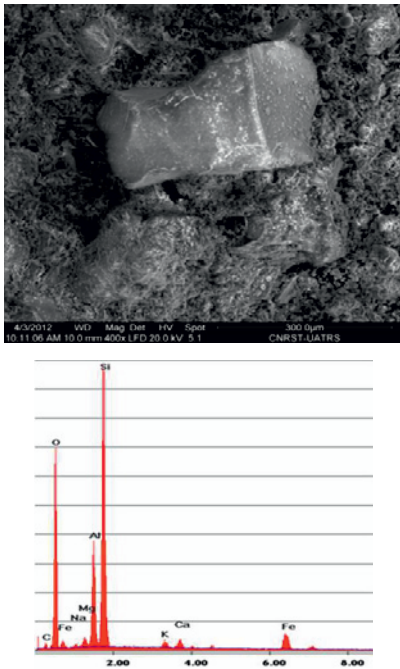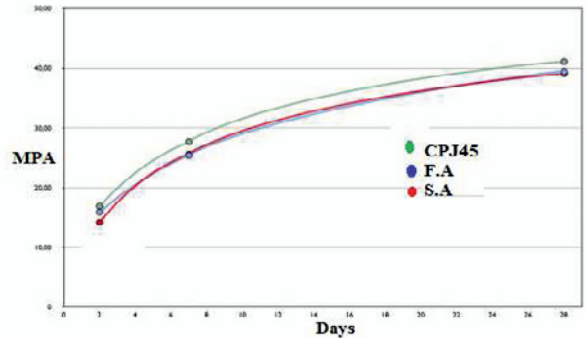

Fig. 6: Image by SEM and EDAX analysis of bottom ash showing a quartz particle (Photo.3)

Table.4 The evolution of mechanical strength of Cpj45 with the ash added

Ciments	Bending strength (MPa)			Compressive strength (MPa)		
	2d	7 d	28d	2d	7d	28d
Addition of fly ash to CPJ$_{45}$						
CPJ 45	3.7	4.8	7.1	15.9	25.4	39.4
CPJ$_5$45	3.8	5.2	6.9	15,4	25,9	38.8
CPJ$_7$45	3.6	4.9	7.2	16,9	27,7	41.1
CPJ$_{10}$45)	3.2	5.2	7	14,3	25,9	37.9
CPJ$_{15}$45	2.7	4.4	6.8	13	23,1	35.5
CPJ$_{20}$45	3	4.2	6.5	12.3	20.5	33.3
Addition of oil shale ash to CPJ$_{45}$						
CPJ 45	3.7	4.8	7.1	15.9	25.4	39.4
CPJ$_5$45	3.2	4.9	6.5	14.3	25.5	38,5
CPJ$_7$45	3.2	4.6	6.9	14.2	25.6	39.1
CPJ$_{10}$45	3	4.9	7.3	14.9	27.6	42.7
CPJ$_{15}$45	3.2	4.8	6.7	14.4	26.8	35.4
CPJ$_{20}$45	2.3	4.3	6.6	9.6	22.1	30.5
Addition of bottom ash to CPJ$_{45}$						
CPJ45	3.7	4.8	7.1	15.9	25.4	39.4
CPJ$_5$45	3.8	4.8	7.8	19.4	29.3	44.1

strength. Canpolat et all [17] have prepared a series of cement by adding zeolites and zeolites or bottom ash and fly ash. They found that the cement produced by perforation of zeolites and 5% of bottom ash has good compressive strength relative to the cement prepared by adding 5% of zeolites and 5% of fly ash. These results show that the addition of 5% of bottom ash contributes to the improvement of the compressive strength of cement compared to the same percentage of of fly ash.

Figure 9 shows that the cement that we have prepared with 5% of bottom ash has a compressive and bending strength at 28 days higher than cements prepared by the

Fig.7. Evolution of the compressive strength of the cementas a function of time with 7% of different ash added
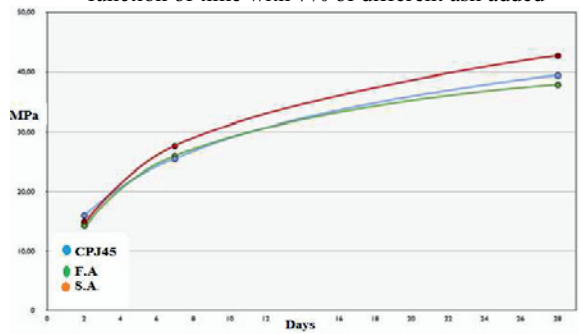

Fig 8. Evolution of the compressive strength of the cement as a function of time with 7% of different ash added
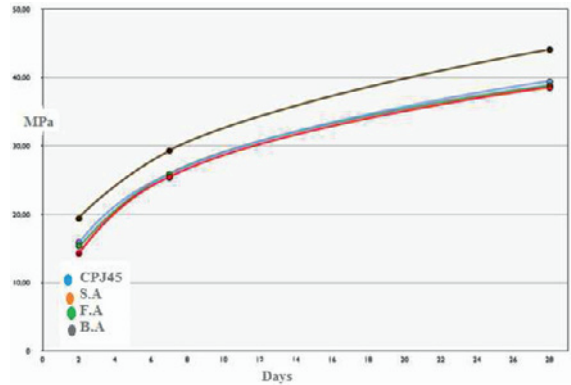

Fig 9. Evolution of the compressive strength of the cement as a function of time with 7% of different ash added
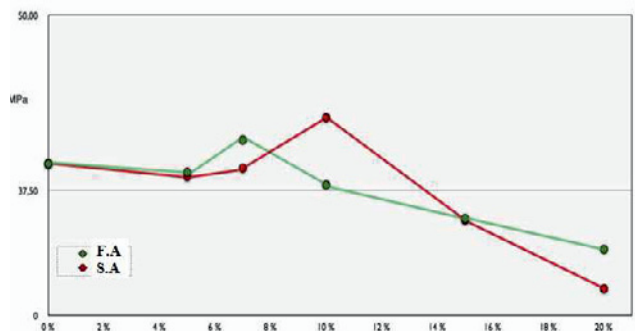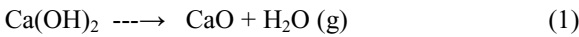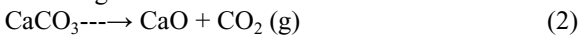

Fig. 10: Evolution of 28 days compressive strength with the substitution of cement by different percentage of F.A or S.A

3.6 Differential Scanning Calorimeter (DSC)

DSC analysis was performed for anhydrous an three days hydrated samples for the prepared cements that have the best 28 days compressive strength (by adding 5% of bottom ash, 7% of fly ash or 10% of oil shale). Each DSC curve of hydrated cements (Fig.11) shows three endothermic peaks. The first peak between 100 and 150°C is due to dehydration of CSH. Generally young age cements show gradual loss of two types of water molecules (free water and bound water in CSH) giving two secondary peaks at around 100°C [18], so we can attribute the left shoulder of the first peak of the three types of cement to the first dehydration. We note that the cement prepared by adding 10% of oil shale is dehydrated to a slightly greater temperature than cements prepared by adding 5% and 7% of bottom or fly ash.

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

$$Ca(OH)_2 \longrightarrow CaO + H_2O \text{ (g)} \qquad (1)$$

At 600°C we observe a descent heat flux giving a third peak, which corresponds to the lost of CO_2 during the decomposition of calcium carbonate according to the following reaction:

$$CaCO_3 \longrightarrow CaO + CO_2 \text{ (g)} \qquad (2)$$

Calcium carbonate may be present in the cement paste for two reasons: The cement may contain a certain percentage of calcite from limestone added during the grinding of clinker or from the carbonation of free lime present in the cement paste. Since the latter process is slow and is only possible for cementations matrix of advanced age, and under certain environmental conditions, we do not consider this explanation in our case .Our study covers very young age cement pastes (3 days).
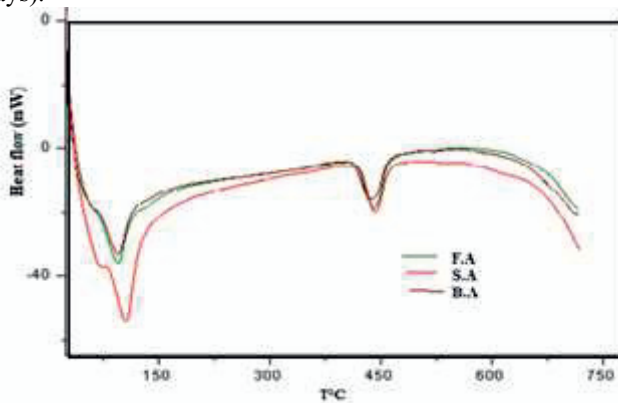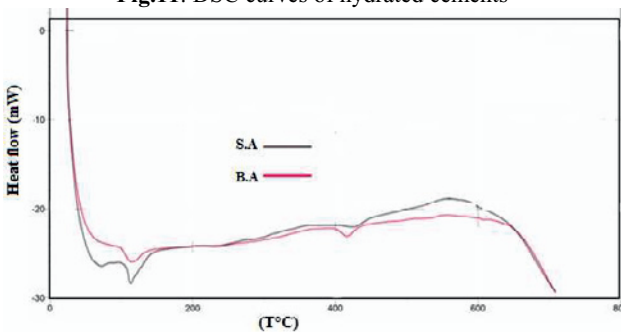

Fig.11: DSC curves of hydrated cements

Fig. 12: DSC curves of anhydrous cements

The DSC curve of anhydrous (Fig.12) cement presents three endothermic peaks. The first peak between 100 and 150°C, with a maximum at 110°C may be due to the dehydration of the water absorbed, or to the decomposition of gypsum used to prepare the cement [19].The second peak with the smaller intensity can be interpreted as dehydration of $Ca(OH)_2$ formed in contact with moisture in the air, despite the precautions taken for the conservation of cement [20]. We note that the peak of the cement prepared by adding 5% of bottom ash appears at 420°C is higher than that of cement prepared by adding 10% of oil shale ash (410°C). The third peak located beyond 600°C is due to the decomposition of the calcite of the limestone added during grinding of the clinker

Conclusion

The study of physico-chemical characterization of fly ash, bottom ash and oil shale ash and the influence of their addition on the mechanical proprieties of the CPJ_{45} cement. XRD showed that bottom ash is constituted of quartz and mullite, the same crystals are found in fly ash with the hematite and magnetite XRF. These ashes have de composition of a class F ash with poozzolanic properties.

Oil shale ash is composed of quartz, anhydrite, gehlenite, wollastonite and periclase, thus belongs to the class C ash and possesses hydraulic and poozolanic properties. We observe with SEM that the microstructures of bottom ash are composed of big particles with spherical or irregular shapes. Analysis coupled with an electronic microscope provided some information about the major elements that constitute our samples. The dehydrations of anhydrous and three days hydrated cement were examined by DSC. For hydrated cements we noticed endothermic peaks related to the dehydration of CSH, CH and decomposition of carbonate. The study showed that the mechanical properties (to 28d) of CPJ45cement by adding different proportions of fly ash, bottom ash and oil shale ash were improved. The cements studied have their maximum mechanical resistance with the addition at 5% bottom ash, 7% of fly ash or 10%d of oil shale ash. the addition of 5% of the bottom ash greatly improves the mechanical properties of the cement by 4.7 MPa for compressive strength and 0.7 MPa for bending strength.

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