Effect of a partial replacement of Portland cement by date seeds on the mechanical and chemical behavior of the mortar

Chiraz Elazizi [a], Halim Hammi [a], Wiem Marzouk [b], Hatem Majdoub [b*] and Adel M'nif [a]

[a] *Useful Materials Valorization Laboratory, National Centre of Research in Materials Science, Technologic Park of Borj Cedria, B.P. 73, 8027 Soliman, Tunisia*
[b] *University of Monastir, Laboratoiry of Interfaces and Advanced Materials (LIMA), Faculty of Sciences of Monastir, Bd. de l'environnement, 5019 Monastir, Tunisie*

(Received: 02 Juillet 2017, accepted: 01 November 2017)

Abstract: The aim of this experimental study is a comparative analysis of the behavior of cementitious mortars developed from a mixture of CEM II / A-L 32.5N and different proportions of the dates seeds (DS) from Phoenix Dactylifera L. and therefore highlight the influence of DS on the strength and durability of the mortars and try to bring a better understanding about the chemical reactions responsible for the increase of sustainability. Techniques such as X-ray diffraction and Scanning Electron Microscopy were used to determine the structure of the new formulation. After curing specimens at 28 days in water, they are immersed in the same concentration acid solutions of 5% (HCl, CH_3COOH). Mass measurement tests are performed at different ages. The results are used to demonstrate the beneficial effect on the compressive strength and the durability of such DS addition, while having a natural setting retarder or accelerator according to the addition rate.

Keywords: Sustainability, Mortar Biomass (Dates Seeds), compressive strength, acid attack, setting time.

INTRODUCTION

In the cement industry, looking for a less expensive binder incorporating industrial waste and natural resources has become a major concern for the deficit level in the manufacture of Portland cement and its climate issues. Different types of additions such as natural pozzolan, fly ash, silica fume, blast furnace slag and calcareous filler among others are usually included.

The incorporation of these active and inert mineral additives in the binder can improve their characteristics as has been highlighted in several studies [1-4].

Among these resources the biomass could exert an important role, since it is renewable, CO_2 neutral energy resource and its by-products are increasingly used worldwide.

Utilization of agricultural by-products substitutes for natural resources provides an alternative for natural minerals [5,6].

Most of the papers are focused on the feasibility of using biomass fly ash as a partial cement replacement material [7,8]. While, only a few papers deal with the valorization of the agriculture by-products in cement based materials [9].

For these reasons, the addition of Date Seeds (DS) in mortar due to its wide availability in Tunisia and high polysaccharides content and consequent potential as organic additive [10-13].

This study investigates the effect of the partial substitution of a quantity of Portland cement by Date Seeds (DS) powder on the mechanical strength, setting time and durability towards acid environment elaborate mortars. Moreover, we will compare the behavior of prepared mortars with only cement (CEM II 32.5 N) and the mortars containing different dosages of DS.

Crystalline phases were performed by XRD analysis with a Philips PW 3050/60 2q goniometer and a PW 3373/00 copper cathode, at a scanning speed of 2°/min (Fig. 1), and the results of DRX (Fig. 7) are fitted using X'pert High score software.

* Corresponding author, e-mail address: hatemmajdoub.fsm@gmail.com

Table I. Chemical composition of the DS powder used (the range of the fiber fraction is expressed in grams per 100g of dry matter).

Date seeds/mortar dry mixture weight ratio (%)	Water/dry mixture Weight ratio (%)	Methods
Solubility in hot water (%)	11.2±0.1	(Tappi T264 om 88, 1988) [15]
Solubility in ethanol-toluene (%)	12.1±0.01	(AOAC Method 920.39, 1997) [16]
α-cellulose (%)	25.1±0.1	(Pettersen, 1984) [17]
Kalson lignin (%)	22.6±0.1	Klason and TAPPI (T22 om -88, 1998) [18]
Hemicelluloses (%)	26.1±0.1	(Wise et al, 1946) [19]
Ash (%)	1.5±0.1	(AOAC Method 942.05, 1995) [20]

The date stones are clearly a lignocellulosic material whose main components are hemicellulose, α-cellulose and kalson lignin.

MATERIALS AND METHODS

Portland cement type (CEM II A 32.5) was used for the preparation of samples. This type of cement is resulting from the fine grinding of Portland clinker at least 80%, 20% more filler limestone and setting regulator (gypsum) in appropriate proportion, according to the AL-Tunisian standard NT 47-1 and European standard EN 197-1.

The material used for the preparation of mortar comes from Borj Hfaidh (Nabeul) quarry. The maximum size of grains of sand used is 600 µm. The particle size distribution (PSD) is measured by a laser particle MICROTRAC S3500. The particle size distribution shows an average fineness, parameter underpinned by a high percentage, 50% of particles smaller than 300µm and 80% less than 400µm. About 95% of the particles are characterized by a diameter smaller than 550 µm.

The material used is a powder ground DS provided from the variety of the more common dates of Tozeur region (Tunisia) namely: 'Deglet Nour' (*Phoenix Dactylifera L.*)

Dates are pitted manually and macerated cores in plain water for 24 hours and then thoroughly rinsed to remove the maximum of impurities and finally dried in an oven at 75 ° C for 24 hours [14]. Seeds pulverized using a mill (Retsch R200) gave a homogeneous mixture which constitutes the date stones' flour. The ground material is kept in tightly closed bottles to use as raw material in our work.

Separation representative fractions of the material obtained are performed by a screening machine type Retsch. After several preliminary tests, it was decided to use in this study, DS powder's particles size under 600 µm.

The chemical composition, using various standard methods, of the ground material obtained from the DS has been established and the results are reported in Table I.

Crystalline phases were performed by XRD analysis with a Philips PW 3050/60 2q goniometer and a PW 3373/00 copper cathode, at a scanning speed of 2°/min (Fig. 1), and the results of DRX (Fig. 7) are fitted using X'pert High score software.

The date stones are clearly a lignocellulosic material whose main components are hemicellulose, α-cellulose and kalson lignin.

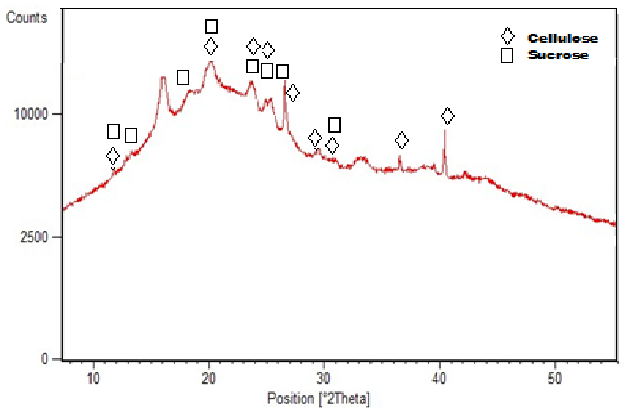

Fig. 1. XRD analysis of the DS powder.

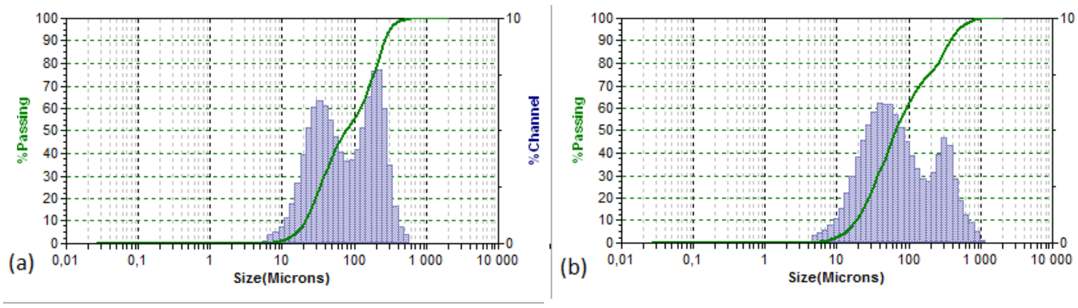

Fig. 2. Particle size distribution of the DS powders: (a) DS powder ≤ 212µm and (b) DS powder ≤ 600µm.

The particles size distribution (Fig. 2) of the DS powder shows that 50% of particles smaller than 80µm and 75% less than 200µm for the first fraction tested (≤ 212µm) and at least about 49% of DS particles are less than 300µm for the second one (≤ 600µm).
The mortar specimens are made according to the European standard 196-1 [21] with constant mixing water rates: W/C = 0.5. In this type of samples, we have incorporated the ground DS in different percentages (0%, 1%, 2.5% and 4%) and different particle sizes (≤212µm, ≤600µm).
The effect of ground DS addition on the mechanical strength development of cement based materials was evaluated on 40x40x160 mm mortar specimens dimension after demolding at 24 hours and 28 days cure underwater.
Compressive strength measurements were performed on three replicate specimens (4x40x40mm) after curing time of 28, 90 and 110 days at 20°C.
Cube specimens are immersed in the same concentration solution (w/w) of 5% HCl and 5% CH_3COOH for the characterization of resistance due to acid attack after being cleaned 3 times with fresh water to remove the altered mortar and then dried for ½ hour.
Mass measurement tests are then performed after 1, 7, 14, 21, 28, 35 and 42 days according to the ASTM C267-96 standard. The degree of attack is measured by the Mass Loss (ML) given by the formula (1):

$$ML(\%) = \frac{M1-M2}{M1} * 100 \quad (1)$$

where M1and M2 are the masses of the specimens before and after immersion, respectively.
The setting behavior of blended and Portland cements was evaluated by measuring the initial and final setting times of pastes made with normal consistency (W/C = 0.26) according to EN 196-3 test method (vicat apparatus).
The seven-mortar series thus obtained are designated by E0 (ordinary mortar), E1 (1% ground DS ≤212µm particle size), E2 (4% ground

Table II. Results for compressive strength of ordinary mortar and DS added mortars.

Samples	% Added	Granulometry (µm)	Compressive strength (MPa) (28days)
E0	0	-	28.625
E1	1	≤212	42.460
E2	4	≤ 212	38.687
E3	1	≤ 600	38.647
E4	4	≤ 600	40.392
E5	2.5	≤ 212	32.236
E6	2.5	≤ 600	38.102

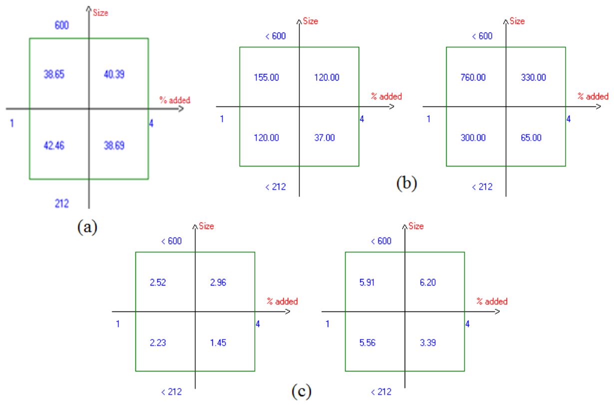

Fig. 3. Study of interaction X1 * X2 effects on (a) the mechanical strength, (b) the initial and final setting time and (c) the mass loss after 28 days of acetic and hydrochloric acid attack.

DS ≤212µm particle size), E3 (1% ground DS ≤600µm particle size), E4 (4% ground DS ≤600µm particle size), E5 (2.5% ground DS ≤212µm particle size) and E6 (2.5% ground DS ≤600µm particle size).
All samples of different mortars are kept under the same conditions of temperature and humidity.

RESULTS AND DISCUSSION

1. Design of Experiments

We studied the effect of adding the ground dates seeds (DS) on the setting time, mechanical strength and durability performance towards acidic environment mortars made with Portland cement.
The experiments, conducted on a full factorial experimental design 2^2 by varying two factors namely the percentage of DS addition and its size.
The adjustment range of these two factors is delimited after a preliminary study which gives us the available variation range.

2. Mechanical strength

The changes in mechanical properties of Portland cement mortars due to the addition of ground date seeds (DS) to the mix have been studied.
Compression has been determined in relation to the amount of biomass material added to the mix.
From the results of Table II, we note a clear improvement in mechanical strength for all samples compared to the ordinary mortar E0 and particularly an increase of 48.33% for sample E1 compared to E0.

Fig. 3 shows the effect of the studied factors (percentage added of DS and granulometry) on the responses by Pareto diagrams.
In the case of negative coefficients, the mechanical strength decreases when the value of the parameters moves to the upper limit, when the percentage of substitution increases to 4% and the particle size of the substituent DS passes to 600µm. They reduce the mechanical strength consistently because of the decrease of the cementitious phase, and because the porosity increases by increasing the granulometry, which weakens the structure. However, the interaction between the 2 factors increases the mechanical resistance.
Nevertheless, the two factors under consideration have the same effect on the studied response.
The analysis of the association of different elements is available in the diagrams' form. The answer of experience is so interpreted: when the factor changes from its lesser state to its upper state, it has a positive effect if the response increases and a negative effect if the response decreases. The interactions between two factors express antagonistic effects with a negative coefficient and synergistic effects with a positive coefficient.
In our case, when the particle size decreases to 212µm, the mechanical resistance increases for specimens at 1% of DS addition (E1, E3). However, 600µm dimensional size particles for the DS particle seem to be better for 4% of DS addition (Fig. 3).

3. Setting time

The results of variation of the initial and final setting times of different samples summarized in

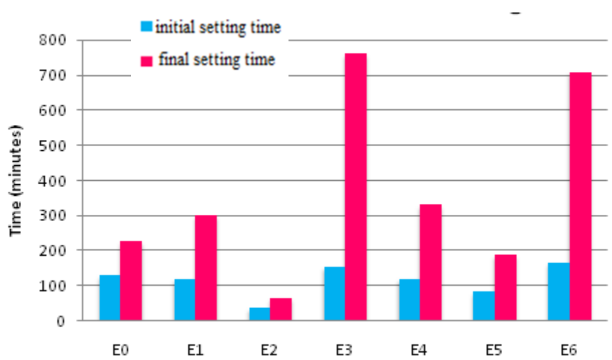

Fig. 4. Variation of the initial and final setting times of the prepared samples.

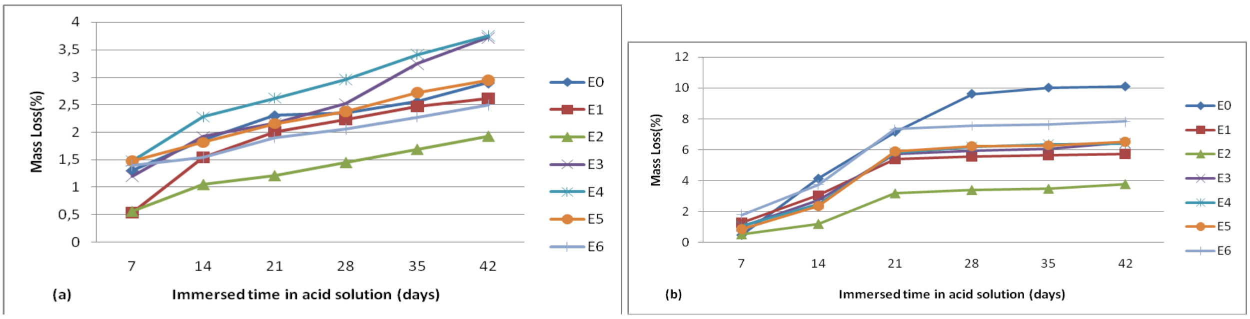

Fig. 5. Mass loss percentage of DS mortars immersed in (a) acetic acid and in (b) chloric acid.

Figure 4 show a fluctuating variation according to the rate of substitution and the particle size. It is then found a retarding effect for samples E1, E3, E4 and E6 and an accelerator one for E2.

For the same particle size, the increase of percentage of DS replacement reduces the setting time of DS mortar. It thus acts as a setting time accelerator. Whereas, for the same added percentage, particle size increasing plays the role of a retarder. However, the retarding effect predominates when it's about the interaction between the two factors as it is clear in Figure 3. In fact, the high relative content of hemicellulose and water soluble polysaccharides in the DS retards the cement hydration process [13].

4. Chemical resistance

The results of the study dealing with the acid attack of ordinary mortar (E0) and mortar with DS (E1, E2, E3, E4, E5, E6) addition by mass measurement tests and the period of immersion in 5% acetic and chloric acid solutions are summarized in Figure 5.

For the acetic acid, which is an organic acid forming calcium acetate with calcium hydroxide which is very bit soluble in water (1) [22].

$$Ca(OH)_2 + H_3CCOOH \rightarrow Ca(H_3CCOO)_2 + H_2O \quad \textbf{(1)}$$

It was found that, after 42 days of immersion in the solution of 5% CH_3COOH, the mass loss of the mortars mixed with 1% until 4% DS replacement was lower than the ordinary mortars. Thus, the addition of DS allows more water to absorb into the particles and promotes the disintegration of acid ions in the mortar texture matrix (2). As the DS replacement and the size of particles increases, the porosity and acid corrosion increases, too (Fig. 3).

$$H_3CCOOH \rightarrow H_3O^+ + H_3CCOO^- \quad \textbf{(2)}$$

For the hydrochloric acid (HCl) which is an inorganic acid and more detrimental to concrete and mortar as organic acids, which form with the $Ca(OH)_2$ contained in the paste hardened cement, the calcium chloride ($CaCl_2$) readily soluble compounds in water (3) [23]:

$$Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2\ H_2O \quad \textbf{(3)}$$

Similarly, it was retaining that until 42 days of immersion in the solution of 5% HCl, the mass loss, for all specimens with DS addition, was lower than ordinary mortar.

The replacement of DS affected the hydration reaction and resulted in a lower amount of calcium hydroxide. For this reason, the reaction between hydrochloric acid and calcium hydroxide ions decreased. The higher water absorbability of DS powder resulted in lower volumes of water in the capillary pores, thus reducing the dissolution of chloric ions [24] and so decreasing the corrosion. However, as the percentage of DS replacement and the size of particles increases, the mass loss increases, too (Fig.3).

Ordinary Portland cement (OPC) mortar is susceptible to chloride and acetic acid attacks due to its alkaline nature. The high amount of CaO in OPC and the released $Ca(OH)_2$ makes it vulnerable. The components of the hydrated cement paste break down during contact with acids. The most prominent is the dissolution of Ca $(OH)_2$ that the chemical reaction involved in acid attacks can be given as

$$2\ HX + Ca(OH)_2 \rightarrow CaX_2 + 2\ H_2O \quad \textbf{(4)}$$

where X is the negative ion of the acid.

The deterioration of the mortar depends on the porosity of the cement paste, the concentration of the acid and the solubility of the acid calcium salts

(CaX_2). Chloride and acetic acids are very aggressive as their calcium salts are readily soluble. Mass losses in mortar samples occur due to the effect of HCl and CH_3COOH solutions. Also, due to the conversion of calcium hydroxide, as it is readily soluble in acid environment, to Calcium Silicate Hydrate (C–S–H) and ettringite crystal, which increases the acid resistance of the DS specimens [25-28].

5. Optimum characteristics

In order to get a better composition of a new binder to obtain considered added value, it is found that, specially, the two samples (E1 and E2) have increased their ability to resist to strong and weak acids, besides the increase of the mechanical resistance with two different effects on the hydration of cement. However, it is estimated that the formulation of the E1 specimen, allowed us a comparable effect to the ordinary mortar with an increase of 48.33% in the compressive strength, a lower mass loss of 22% for the strong acid attack, a same mass loss rate for the weak acid attack, while having a retarding effect on the hydration of cement (74 min).

This optimum will be characterized by study the evolution of the compressive strength in the time, the XRD and also the SEM.

5-1. Compressive strength

The evolution of the compressive strengths for the mortars is shown in Fig.6. The measurements are done for the period lying between day 28 and day 110. It can be observed that the compressive strength of the mortar increases steadily with the different ages of samples. The date seeds are high in holocellulose, α-cellulose and Kalson lignin, thus considered as a lignocellulosic material suitable for improving mechanical strength, structural and sustainable properties [29-32].

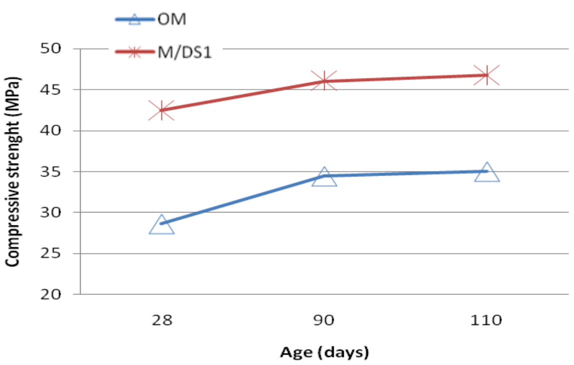

Fig. 6. Variations of compressive strength at different ages of ordinary mortar (E0) and mortar with 1% of DS (E1).

5-2. X-rays Diffraction

To investigate the chemical interaction between the cement material and the DS, XRD diffractogram analysis of E0 and E1 was conducted.

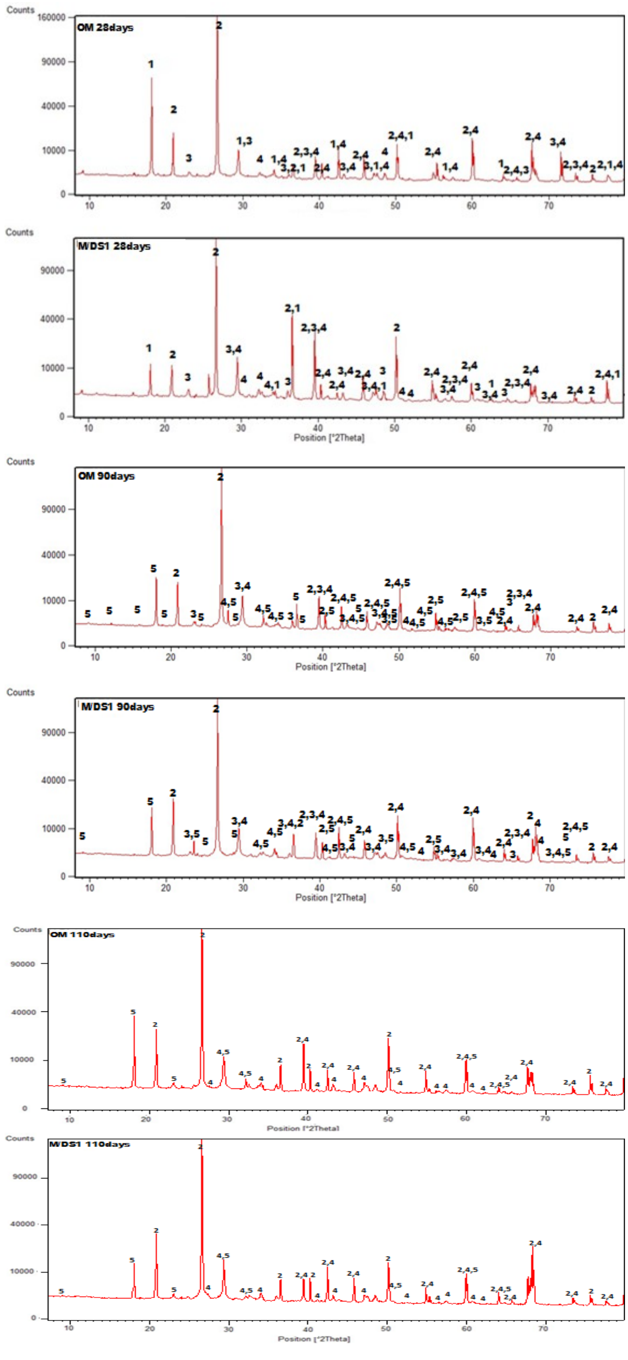

Fig. 7. Comparative DRX of 28, 90 and 110 days cured Cement-DS 1% pastes. The phases identified were (1) Portlandite $Ca(OH)_2$, (2) Quartz SiO_2, (3) Calcite $CaCO_3$, (4) Alite (C_3S) Ca_3SiO_5 and (5) Ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$).

Fig.7 shows the XRD diffractograms of E0 and E1 after 28, 90 and 110 days. It can be observed that these diffractograms does not indicate significant difference in terms of crystalline structures concerning the binding materials and it does not exhibit any other phases than those observed for the E0. In fact, the analysis permitted to observe that C-S-H possesses high crystallized hydrates, namely the ettringite and the portlandite.
Also, the diffractogram of E1 shows a high hydration. A rearrangement of the crystalline structure occurred therefore during cement hydration, as absorption bands characterizing anhydrous clinker, are replaced by the hydration particles. However, the addition of DS to the cementitious matrix influences the kinetics of the reaction.
In details, the ettringite reaches its highest peaks equal to 18.09, 50.02 and 60.02 and calcite $CaCO_3$ reaches its highest peak at 2q equal to 29.41.

5-3. Scanning Electron Microscope observations

Scanning Electron Microscope (SEM) tests are performed using FEI (ESEM) the apparatus. This part of the study focuses upon visualizing the E0 and E1 morphologies after different ages, as shown in Fig. 8. At room-temperature and after 28 days,

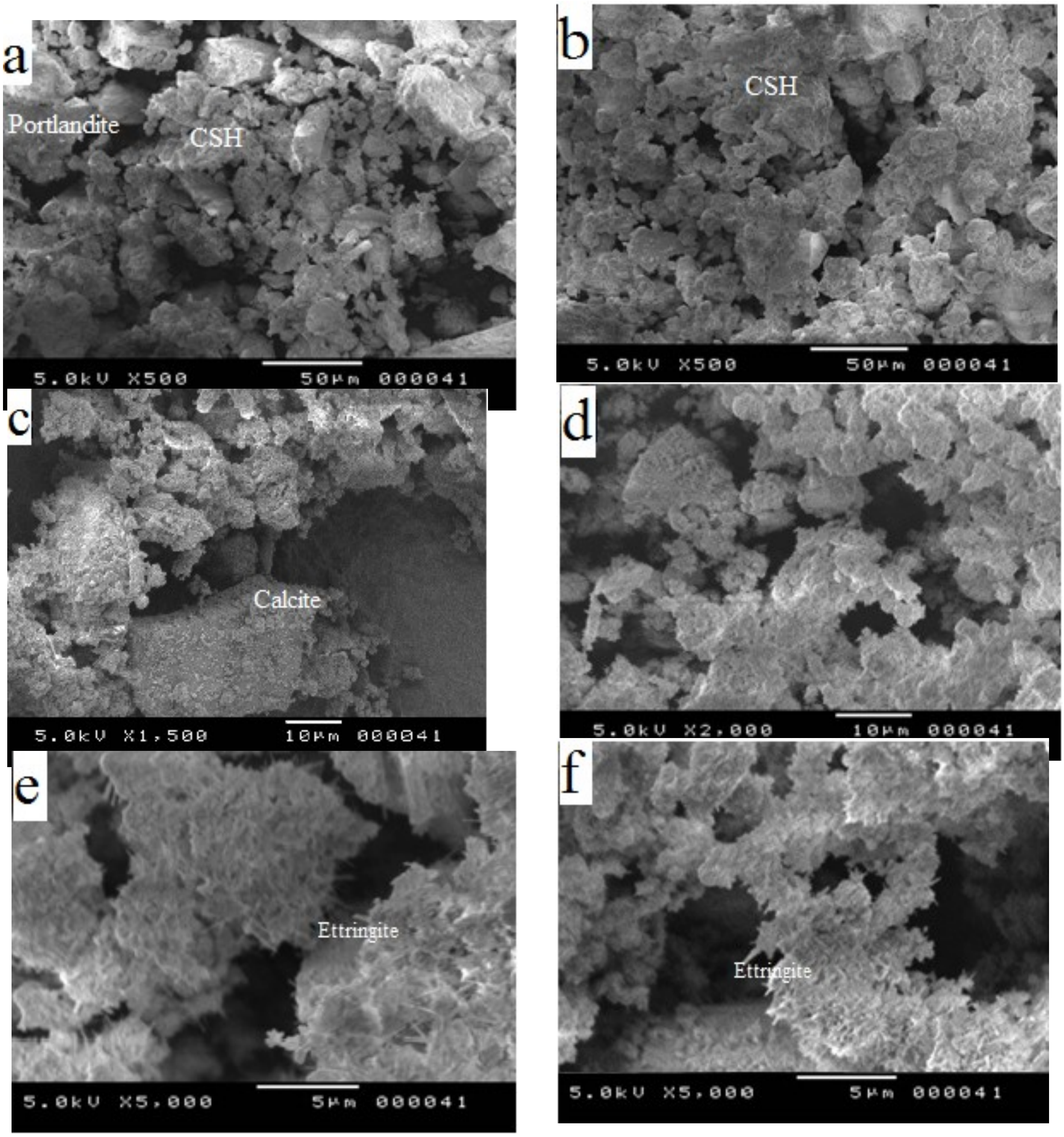

Fig. 8. SEM photographs of E0 (a,c,e) and E1 (b,d,f) after 28, 90 and 110 days, respectively.

SEM images show that E0 represents the appearance of hydrated phases such as large portlandite crystals and a gel-like appearance around the cement grains depicted as the amorphous CH gel. Ettringite needles in colloidal form with CH were also visible. Similarly, E1 is characterized by the appearance of a particle of DS surrounded by cement. Besides, same phases were identified with more compact amorphous gel morphology, which is responsible for the increase of the mechanical strength.

These results are in perfect concordance with those obtained from the XRD spectra analysis.

CONCLUSIONS

The results presented in this paper have shown a good potential for the use of 1% of the powder of the DS with particle size ≤212µm mortars based Portland cement. The main comments obtained are listed below. The DS as a lignocellulosic material, allowed an increase in the mechanical strength. It can be concluded that up to 4% with particle size ≤212µm, the DS can be incorporated as a substituent of Portland cement in mortars. Only the setting time varies to have a natural setting accelerator and better effect on the durability. The mechanical strength of the mortar with 1% DS (E1) was 42.460 MPa at 28 days. This value was 48.33% higher than the 0% DS mortar, at the same water/binder ratio. The DS mortars (E1) have shown excellent performance when exposed to hydrochloric and acetic acids with varying immersion durations which is very promising in producing current and future green materials to achieve durability without using toxic chemicals.

DRX study shows that there is no generation of new material by introducing DS. There is only a physical reaction between cement and biomass. SEM observations permitted to investigate the state of the cement matrix after incorporation of 1% of DS powder which caused more compact structure and therefore the increase of the mechanical and durability characteristics.

REFERENCES

[1] Desarnaud E., Ando S., Desbarbieux T., Prebay Y., *Atelier Changement Climatique* ; Les enjeux du développement durable au sein de l'Industrie du Ciment : Réduction des émissions de CO2. (**2006**) 45p.

[2] Chindaprasirt P, Rukzon S. Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk as fly ash mortar. *Constr Build Mater* **2008**; 22:1601.

[3] Vaicˇiukyniene˙ D, Vaitkevicˇius V, Kantautas A, Sasnauskas V. Utilization of byproduct waste silica in concrete-based materials. *Mater Res* **2012**; 15:561.

[4] Kanning RC. Utilizacao da cinza de folha de bananeira como adicao em argamassas de cimento Portland. (Thesis). Brasil: Universidade Federal do Parana; **2013**.

[5] K.L. Lin, The influence of municipal solid waste incinerator fly ash slag blended in cement pastes, *Cement and Concrete Research* 35 (**2005**) 979-986.

[6] Malek B., Iqbal M., Ibrahim A., Use of selected waste materials in concrete mixes, *Waste Management* 27 (**2007**) 1870-1876.

[7] Campbell AG. Recycling and disposing of wood ash. *TAPPI J* **1990**;73(9):141-3.

[8] Ramos T, Matos AM, Susa-Coutinho J. Strength and durability of mortar using cork waste ash as cement replacement. *Mater Res* **2014**.

[9] Marcos A.S. Anjos, Antonio E. Martinelli, Dulce M.A. Melo. Effect of sugarcane biomass waste in cement slurries submitted to high temperature and pressure. *Materials Science and Engineering* A 529 (**2011**) 49-54.

[10] Ganesan K., Rajegopal K., Thangavel K., *Cem. Concr. Compos*. 29 (**2007**) 515-524.

[11] Wang S., Baxter L., Fonseca F., *Fuel* 87 (**2008**) 372-379.

[12] Cordeiro G.C., Toledo Filho R.D., Tavares L.M., Fairbairn E.M., *Cem. Concr. Res*. 39 (**2009**) 110-115.

[13] Panesar D.K., Shindman B., The mechanical, transport and thermal properties of mortar and concrete containing waste cork, *Cement and Concrete Composites* 34 (**2012**) 982-992.

[14] Haimour N.M.; Emeish S. (**2006**); Utilization of stones Date for Production of activated carbon using phosphoric acid; *Waste Management* 26, 651 -660.

[15] Tappi Test Methods, T 264 om-88, Tappi Press, Atlanta, GA, USA, **1988**.

[16] Official Methods of Analysis of AOAC International 16th Ed., AOAC International, Gaithersburg, MD, USA, *Method* 920.39, **1997**.

[17] Pettersen R., AdvChem Ser., 207, 57 (**1984**).

[18] Tappi Test Methods, T 222 om-88, Tappi Press, Atlanta, GA, USA, **1988**.

[19] Wise L. E., Murphy M. and D'Addieco A. A., *Pap Trade J.*, 122, 35 (**1946**).

[20] Official Methods of Analysis of AOAC International18th Ed., AOAC International, Gaithersburg, MD, USA, Method 942.05, **1995**.

[21] UNI EN 196-1. *Methods of testing cement*. Determination of strength; **2005**. p.1-66.

[22] Hewlett, P., **2006**. Lea's Chemistry of Cement and Concrete. Elsevier, Burlington, MA.

[23] Mouli M., Senhadji Y., Benosman A. S., Khelafi H.. Resistance to acids and penetration of ions chloride of mortars with pouzzolane and fine limestone.

[24] Pavliok, V., Uncik, S., **1997**. The rate of corrosion of hardened cement pastes and mortars with additive of silica fumes in acids. *Cement Conc. Res*. 27 (11), 1731e 1745.

[25] Effect of rice-husk ash on durability of cementitious materials. Gemma Rodríguez de Sensale. *Cement & Concrete Composites* 32 (**2010**) 718-725.

[26] Mehta P, Folliard K. Rice husk ash - a unique supplementary cementing material: durability aspects. In: Proc second CANMET/ACI international symp. Las Vegas, Nevada; **1995**, ACI SP 154-28. p. 531-41.

[27] Wada I, Kamano T, Kawakami M, Maeda N. Effect of highly reactive rice husk ash on durability of concrete and mortar. In: Proc fifth int conference ACI durability of concrete, Barcelona, Spain, ACI SP192-13, vol. 1. **2000**. p. 205-22.

[28] Yu Q, Sawayama K, Sugita S, Shoya M, Isojima Y. The reaction between rice husk ash and $Ca(OH)_2$ solution and the nature of its product. *Cem Concr Res* **1999**; 29:37-43.

[29] Habibi Y, El-Zawawy WK, Ibrahim MM, Dufresne A (**2008**). Processing and characterization of reinforced polyethylene composites made with lignocellulosic fibers from Egyptian agro-industrial residues. *Composites Sci. Technol*. 68(7-8): 1877-1885. doi: 10.1016/ j.compscitech.2008.01.008.

[30] Alemdar A, Sain M (**2008**). Isolation and characterization of nanofibers from agricultural residues - Wheat straw and soy hulls. Bioresour. Technol. 99(6): 1664-1671. doi:10.1016/ *j.biortech*.2007.04.029.

[31] Shaji J, Kuruvilla J, Sabu T (**2006**). Green composites from natural rubber and oil palm fiber: physical and mechanical properties. *Int. J. Poly. Mater*. 55(11): 925-945.

[32] John MJ, Francis B, Varughese KT, Thomas S (**2008**). Effect of chemical modification on properties of hybrid fiber biocomposites. Composites Part A: Appl. Sci. Manuf. 39(2): 352-363.