



Utilization of pulp black liquor waste as a cement admixture

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Abstract

The pulp black liquor waste (PBL), a byproduct from paper-making, is applied as a cement admixture in two types of cement, namely Ordinary Portland cement (OPC) and Portland limestone cement (LPC). The results showed that the water of consistency of cement pastes premixed with PBL was gradually increased with the concentration of PBL while the setting times (initial and final) were decreased. So, it can be used as an accelerator. The compressive strength increased slightly during the early ages of hydration but sharply during the later ages, particularly with those premixed with PBL. The combined water content and bulk density displayed the same trend as the compressive strength, whilst the apparent porosity decreased at all curing times. The IR spectra of cement pastes showed that the intensities of the different peaks of cement pastes with PBL are higher than those of the pure samples. The SEM images proved that the incorporation of PBL with cement did not affect the chemical composition of OPC or LPC hydrates, but it only affected the physical state, shape, size, morphology and crystallinity of the formed hydrates. The 2 wt. % of PBL is the optimum concentration.

Keywords: PBL, OPC, LPC, combined water, bulk density, porosity, Strength, IR, SEM.

1 Introduction

Though the nature and mechanism of action of cement or concrete admixtures have not yet been explained in a satisfactory way up till now due to the huge variety of admixtures, the use of reducing-water soluble polymer admixtures with dispersing, plasticizing and air-entraining effects at a considerably low polymer / cement ratios is very important because these admixtures improve the workability and modify other properties of cement pastes or concrete. Furthermore, they enhance the performance of concrete structures [1-5].

The black liquor, a waste product from Paper Industry, has attracted our attention due to their unique advantages because the it has a high solubility and low viscosity. This makes it more readily available for several applications as initiators. Black liquor is an important liquid fuel in the pulp and paper industry [6]. It consists of the remaining substances after the digestive process where the cellulose fibers have been cooked out from the wood. One of the main ingredients in black liquor is lignin, which is the material in trees that binds wood fibers together and makes them rigid, and which must be removed from wood fibers to create paper [7-11].

[12, 13] reported that some organic admixtures induce physical effects, which modify the bonds between particles and can act on the chemical processes of hydration, particularly on the nucleation and crystal growth. Accordingly, the black liquor constitutes a new and promising admixture.

Generally, the cement admixtures are used in minor quantities as water-soluble polymers, liquid resins and monomers to confer some beneficial effects as reduction of water requirements, improving workability, control setting, accelerating hardening, improving strength, better durability, desirable appearance and volume changes [14, 15]. The traditional water-soluble admixtures employed as cement modifiers are cellulose derivatives including methyl cellulose, carboxymethyl cellulose and hydroxyethyl cellulose, polyvinyl alcohol, polyethylene oxide, polyacrylamide, etc [14]. The wide achievements of cement admixtures converted our attention to look for new suitable admixtures for cement which is the main objective of the study [16, 17]. So, the main objective of the current paper is to study the effect of pulp black liquor, a byproduct from the pulp production industry, on the physico-mechanical properties and microstructure of OPC and PLC cements.

2 Materials and methods

2.1 Raw materials

A waste of pulp black liquor (PBL) from paper industry was provided by Paper Factory, Alexandria, Egypt. The Ordinary Portland cement (OPC) and Limestone Portland cement (LPC) with blaine surface areas of 3300 and 3100 cm²/g were delivered from Helwan and Tourah Cement Companies, Egypt, respectively. Table 1 shows the elemental analysis of black liquor while the chemical compositions of the OPC and PLC cements are listed in Table 2.

Table 1: The elemental analysis of a dry solid black liquor sample

Element	w/w (%)
C	36.40
Na	18.60
S	4.80
H	3.50
K	2.02
Cl	0.24
N	0.14
O (by diff.)	34.30
TOTAL	100.00

Table 2: The Chemical composition of the OPC and LPC cements, wt. %.

Oxides Materials	L.O.I	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	B. S. A cm ² /g
OPC	2.64	20.12	5.25	3.38	63.13	1.53	0.55	0.3	2.54	3300
LPC	6.44	16.10	4.03	3.80	60.10	1.24	0.65	0.26	1.44	3100

The PBL was dissolved in the mixing water with the dosage of 0, 1, 2 and 3 wt % and then added to OPC and LPC cements. The pastes were moulded into one inch cubic stainless steel moulds (2.5 x 2.5 x 2.5 cm³), vibrated manually for two minutes and on a mechanical vibrator for another two minutes. The surfaces of pastes were smoothed with a spatula and then were kept inside a humidity cabinet for 24 hrs at 23 ± 1 °C and 100 % R.H, demoulded and soon cured under water till the time of testing for bulk density, apparent porosity and compressive strength after 1, 3, 7, 28 and 90 days. The samples were denoted as P₀, P₁, P₂, P₃ for OPC and L₀, L₁, L₂, L₃ for LPC.

The standard water of consistency (mixing water) and the setting times (initial and final) of the prepared cement pastes were directly determined by Vicat Apparatus. [18, 19]. The bulk density and apparent porosity [1] of the hardened cement pastes was calculated from the following equations:

$$B. D. (g/cm^3) = W_1 / (W_1 - W_2) \times 1 \quad (1)$$

$$A. P. \% = (W_1 - W_3) / (W_1 - W_2) \times 100 \quad (2)$$

Where, B.D, A.P, W₁, W₂ and W₃ are the bulk density, apparent porosity, saturated, suspended and dry weights, respectively.

The compressive strength [20] was measured by using a hydraulic testing machine of the Type LPM 600 M1 SEIDNER (Germany) having a full capacity of 600 KN and the loading was applied perpendicular to the direction of the upper surface of the cubes as follows:

$$Cs = L (KN) / Sa (cm^2) KN/m^2 \times 102 (Kg/ cm^2)/10.2 (MPa) \quad (3)$$

Where, Cs: Compressive strength (MPa), L: load (KN), Sa: surface area (cm²).

The chemically-combined water content at each hydration age was also determined on the basis of ignition loss [21] as follows:

$$W_n, \% = \frac{W_1 - W_2}{W_2} \times 100 \quad (4)$$

Where, W_n , W_1 and W_2 are combined water content, weight of sample before and after ignition, respectively.

The phase compositions of some selected samples were investigated using infrared spectroscopy (IR) and scanning electron microscopy (SEM). The IR spectra were performed by Pye-Unicum SP-1100 in the range of 4000-400 cm^{-1} . The SEM images of the fractured surfaces, coated with a thin layer of gold, were obtained by JEOL-JXA-840 electron analyzer at accelerating voltage of 30 KV.

3 Results

3.1 Water of consistency and setting times

The water of consistency and setting times (initial and final) of OPC and LPC cements premixed with PBL waste are plotted in Fig. 1. Generally, the water of consistency gradually increased with PBL concentration up to 3 wt. % in both types of cements. Furthermore, the increase of water of consistency by using the same concentrations of PBL with LPC waste was slightly more than that with OPC. The 3 wt. % PBL waste increased the water of consistency from 28 to 31.67 % with OPC and from 28.5 to 32.45 % with LPC. So, the water of consistency was increased by 1.68-13.12 % with OPC and by 4.11-13.85 % with LPC in comparison with those of their blanks.

On the other hand, the PBL waste decreased the setting times (initial and final) either with OPC or LPC. The 3 wt. % PBL waste decreased the initial and final setting times from 140 to 119 min. and from 255 to 231 min. with OPC, but from 148 to 128 min. and from 266 to 148 min. with LPC, respectively. Accordingly, it is clear that the setting times were faster with OPC than with LPC. Hence, it could be concluded that the PBL liquor waste can act as an accelerator for cement pastes [1, 2].

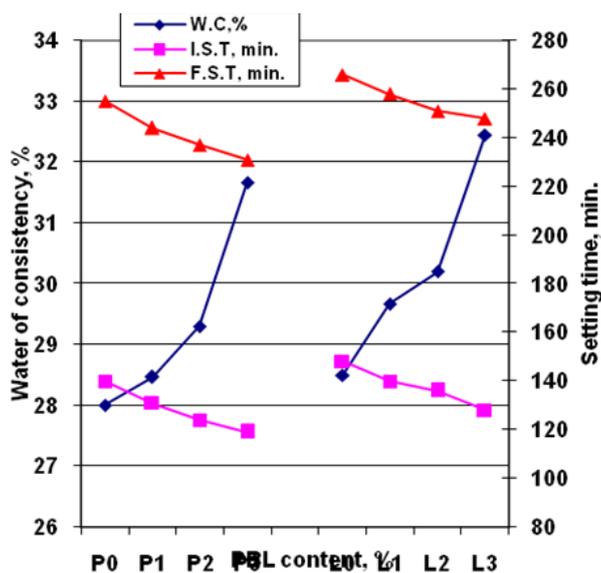


Fig. 1: Water of consistency and setting times of OPC and PLC pastes premixed with 0, 1 and 3% PBL waste

3.2 Bulk density and apparent porosity

The bulk density and apparent porosity of the OPC and LPC cement pastes premixed with 0, 1, 2 and 3 wt. % of PBL liquor waste are illustrated in Figs. 2 and 3, respectively. It is clear that the bulk density gradually increased with curing time while the apparent porosity decreased. This is mainly attributed to the gradual and continual deposition of the formed hydration products in the pore structure of the hardened cement pastes [1, 15]. Moreover, the bulk density was further increased with PBL concentration up to 2 wt. %, whilst the apparent porosity decreased. This may be attributed to the activation and improvement in the hydration process of cement phases by the presence of $\text{Na}(\text{OH})_2$ in the waste liquor and subsequently the amount of hydration products increased compared with those of the blanks [2]. With further increase in PBL concentration as with 3 wt. %, the bulk density was slightly decreased and the apparent porosity increased. So, the higher PBL concentration is not desirable and hence it must be avoided [2, 5].

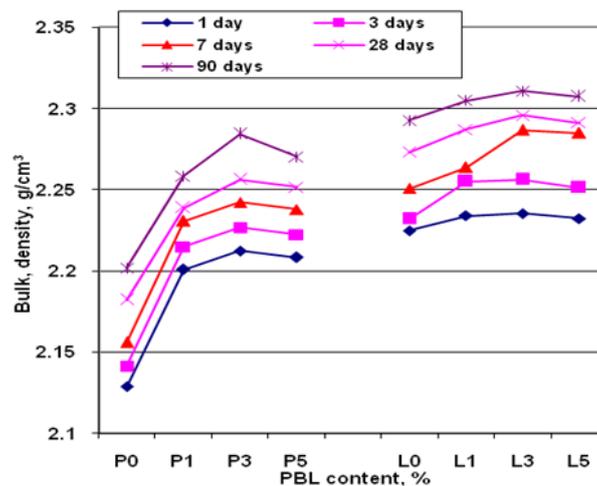


Fig. 2: Bulk density of OPC and PLC pastes premixed with 0, 1 and 3% PBL waste cured up to 90 days

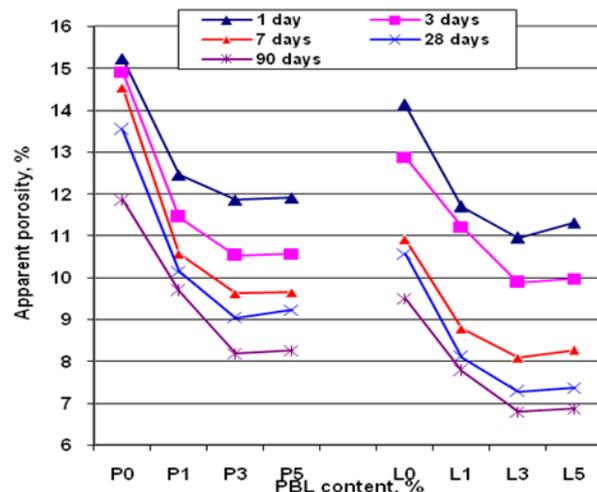


Fig. 3: Apparent porosity of OPC and PLC pastes premixed with 0, 1 and 3% PBL waste cured up to 90 days

3.3 Combined water contents

The combined water contents of the OPC and LPC cement pastes premixed with 0, 1, 2 and 3 wt. % of PBL waste liquor are shown in Fig. 4. Generally, the combined water content of all cement pastes increased with curing time up to 90 days. This was essentially attributed to the gradual and continuous formation of hydration products resulting from the hydration of the main phases of cement, particularly C_3S and $\beta-C_2S$ [1, 15]. The combined water contents increased gradually by incorporation of PBL liquor up to 2 wt. % with both OPC and LPC and then decreased [1, 15 and 22]. The combined water contents of cement pastes with LPC are slightly better than with OPC. This may be due to that the active group in PBL waste (-OH), is more effective with LPC than with OPC pastes [2]. With 3 wt. % of PBL liquor with both types of cements, the combined water contents were adversely affected and hence the higher concentration must be avoided. Also, the PBL waste displayed the same trend with both types of cements at all curing times, but slightly more with LPC pastes [2, 15].

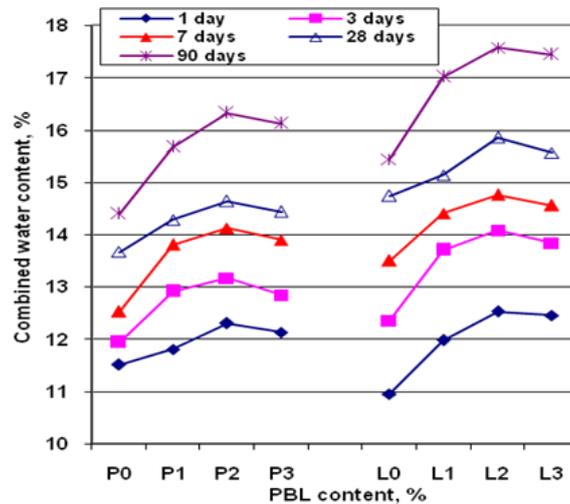


Fig. 4: Combined water content of OPC and PLC pastes premixed with 0, 1 and 3% PBL waste cured up to 90 days

3.4 Compressive strength

The compressive strength of OPC and LPC cement pastes premixed with 0, 1, 2 and 3 wt. % of PBL waste liquor is shown in Fig. 5. The compressive strength of the hardened cement pastes was generally increased with curing time up to 90 days. This is mainly attributed to the continual formation of hydration products which deposited into the pore structure of the cement pastes. So, the apparent porosity decreased gradually and the compactness of samples improved and hence the bulk density increased. This was positively reflected on the compressive strength [1, 15 and 23].

The higher compressive strength for both types of cement (OPC and LPC) compared with those of blank by increasing the PBL waste concentration up to 2 wt. % is mainly due to the high activation effect of the $-OH^-$ group present in the PBL particularly at later ages of hydration. The decrease of the apparent porosity and increase of the bulk density resulted from further increase of the hydration products [4, 5 and 24].

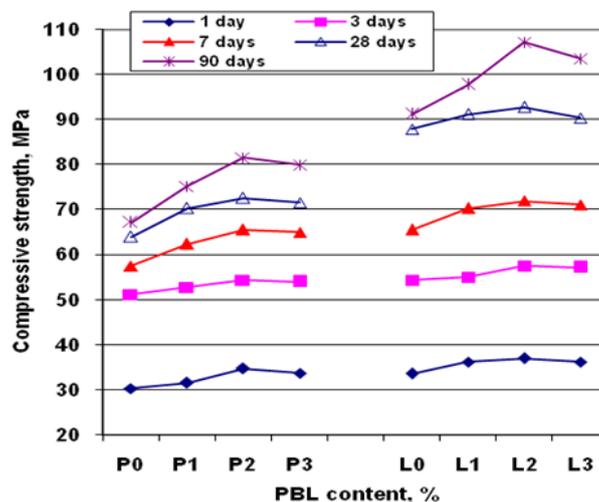


Fig. 5: Compressive strength of OPC and PLC pastes premixed with 0, 1 and 3% PBL waste cured up to 90 days

The addition of PBL waste to cement led to the formation of electrostatic repulsive forces between cement particles negatively charged by the adsorption of the waste onto the cement surface which reduces the interparticle attraction between the cement particles leading to avoid or prevent the flocculation or agglomeration of cement and accordingly a well-dispersed system is obtained [24, 25]. Hence, the slight increase of w/c ratio and the dispersing effects due to PBL waste addition helped to a large extent to improve and enhance the compressive strength. [1] With 3 wt. % PBL waste, the compressive strength was adversely affected. So, the optimum concentration is 2 wt.%, and consequently the higher concentration must be prevented. Fig. 6 demonstrates the dissociation and orientation of the admixture particles as soon as its addition to the mixing water while Fig. 7 shows the adsorption of the admixture particles on the cement grains and its rearrangement to achieve the equilibrium.

Also, the compressive strength of OPC and LPC cement pastes is slightly higher with the incorporation of PBL waste, where it is little higher with LPC pastes than with OPC pastes. Therefore, the activation effect of the PBL liquor increased the rate of hydration which enhanced the cementing characteristics of hardened cement pastes. This often has a positive effect on the mechanical properties. It could then be recommended that the higher concentration of PBL waste must be avoided with both types of cements.

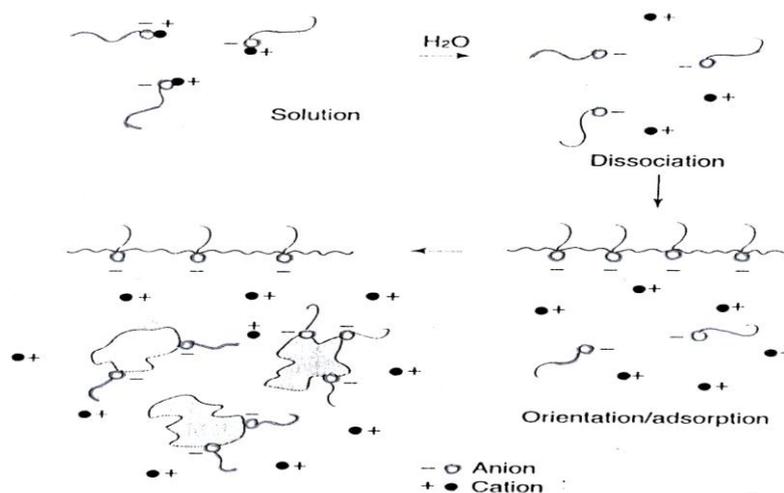


Fig. 6: Surface reactivity and surfactant behavior.

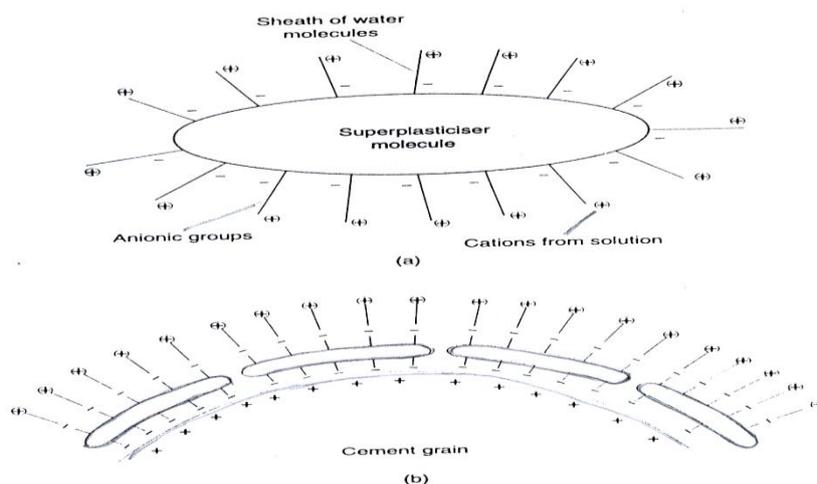


Fig. 7: (a) Representation of an admixture molecule and (b) Mode of adsorption of admixture on cement grain.

3.5 IR spectra

The IR spectra of OPC and LPC cement pastes premixed with 2 wt. % of PBL waste are shown in Figs. 8 and 9, respectively. The sharp absorption band at $3644\text{--}3641\text{ cm}^{-1}$ is related to the free OH^- group coordinated to Ca^{+2} (i.e. free lime). The intensity of the broad absorption band at $3445\text{--}3420\text{ cm}^{-1}$, which was ascribed to the OH^- group associated to H^+ bond that related to the symmetrical stretching frequency of water, increased in presence of PBL liquor. The two bands at 2959 and 2856 cm^{-1} are due to $-\text{CH}_2$ and $-\text{CH}_3$ from the residual organic mixture. The two absorption bands at $1647\text{--}1642\text{ cm}^{-1}$ and $1428\text{--}1425\text{ cm}^{-1}$ are related to the main silicate band involving Si-O stretching vibration bands of CSH, while the band at $1120\text{--}1114\text{ cm}^{-1}$ may be due to CAH. The intensity of the two absorption bands at $989\text{--}983\text{ cm}^{-1}$ and 875 cm^{-1} characterizing CO_3^{-2} and SO_4^{-2} is irregular due to the rate of carbonation or sulphonation of CSH and /or CAH, respectively where the vibrations of CO_3^{-2} are smaller than those of SO_4^{-2} . Also, it is clear that the intensity of the absorption bands of Si-O, CAH, CO_3^{-2} and SO_4^{-2} are slightly higher with PBL waste / cement pastes. The intensities of the characteristic peaks were slightly improved with LPC where a marginal effect with OPC pastes was detected.

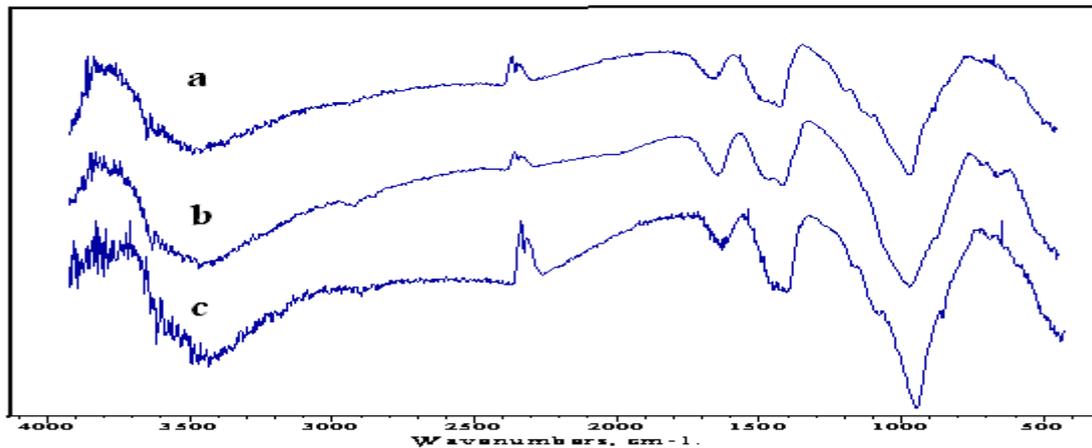


Fig. 8: The IR spectra of OPC pastes cured up to 90 days (a), premixed with 2 % PBL liquor waste (b) and 3 % PBL liquor waste (c).

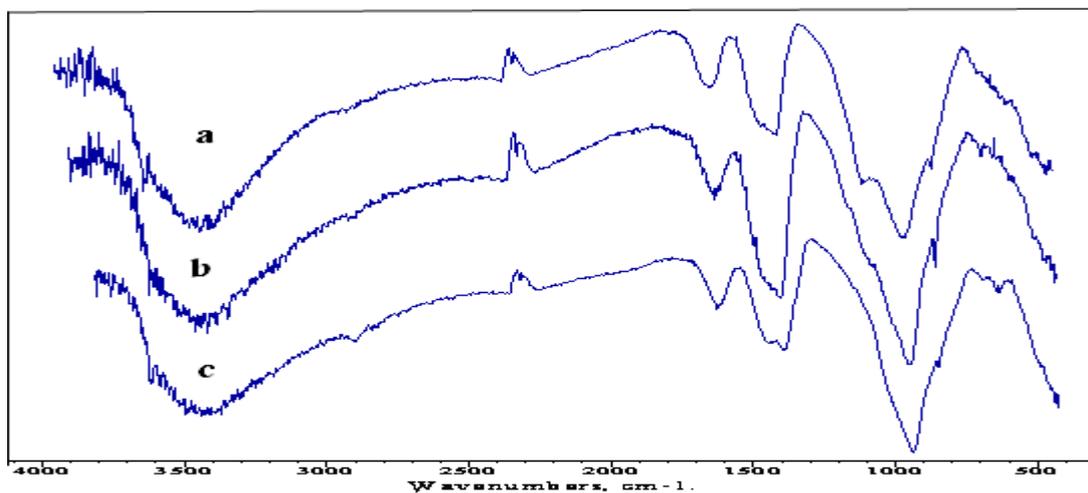
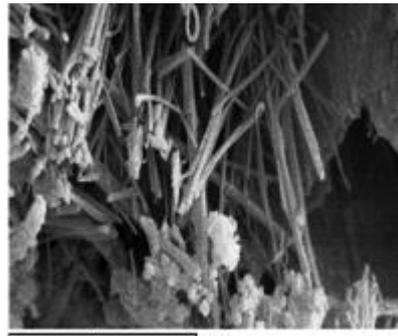


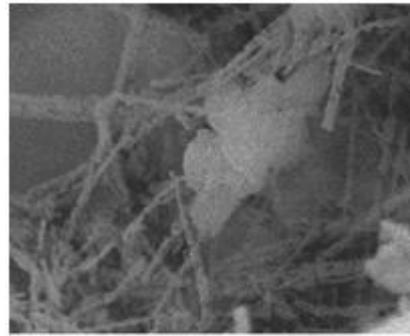
Fig. 9: The IR spectra of LPC pastes cured up to 90 days (a), premixed with 2% PBL liquor waste (b) and 3 % PBL liquor waste (c).

3.6 SEM microscopy

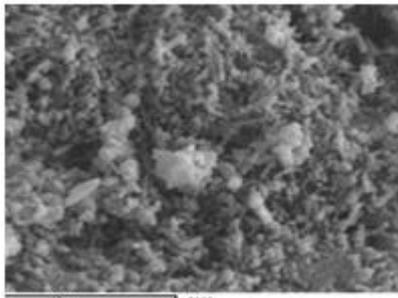
The SEM images of the OPC (a-d) and LPC (e-h) cement pastes premixed with 0, 1, 2 and 3 wt. % of PBL waste are shown in Fig. 10. Generally, the needle-like crystals of ettringite phase ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$) that formed due to the hydration reaction of C_3A with gypsum ($CaSO_4 \cdot 2H_2O$) in presence of water are clearly demonstrated for OPC and LPC blank pastes (Fig.10 a and e). This phase was decreased or disappeared in presence of PBL waste (Fig. 10 b, c, d and f, g, h). This was ascribed to the conversion of ettringite to monosulphate ($C_3A \cdot CaSO_4 \cdot 12H_2O$). These observations indicated a better hydration of cement phases in its presence. The PBL waste also affected the morphology of the $Ca(OH)_2$ crystals, resulted from the hydration of C_3S and/or β - C_2S phases of the cement. Where the $Ca(OH)_2$ crystals represent the weak phase in the binder matrix, the strengthening by PBL waste improves the overall strength of the binder matrix [13, 25]. This in turn was reflected positively on the specific characteristics of the cement, particularly the mechanical strength. On the other hand, the phases that formed with LPC pastes were the same as with OPC pastes but with well-developed crystals, particularly with PBL waste. It could be concluded that the formed phases in case of OPC premixed by PBL waste were the same as with LPC but with different morphologies and crystallinities due the dispersion effect of PBL in both types of cement, where the crystals are larger and more compacted with LPC. So, the PBL waste has more effect on LPC cement pastes than those of OPC pastes.



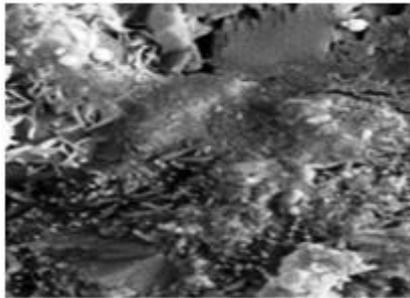
(a) 0 wt. % PBL



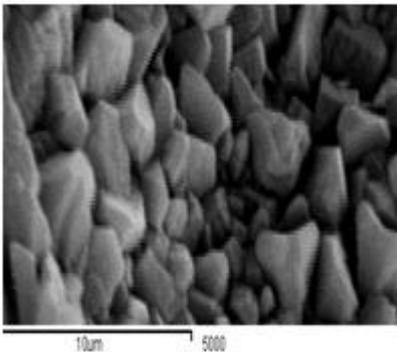
(e) 0 % wt. PBL



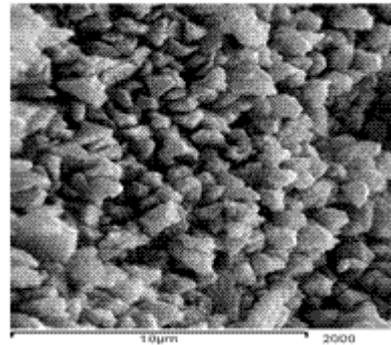
(b) 1 % wt. PBL



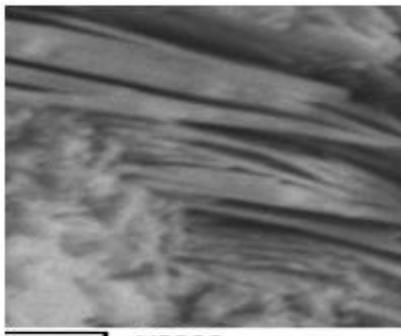
(f) 1 % wt. PBL



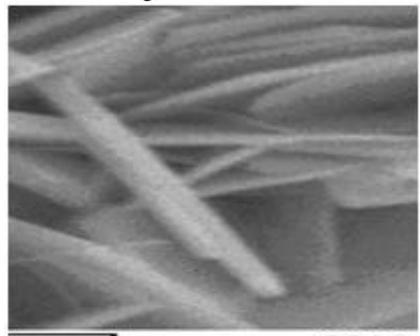
(c) 2 % wt. PBL



(g) 2 % wt. PBL



(d) 3 % wt. PBL



(h) 3 % wt. PBL

Fig. 10: The SEM images of OPC (a-d) and LPC (e-h) pastes premixed with 0, 1, 2 and 3 wt. % PBL waste hydrated up to 90 days.

4 Conclusion

Generally, the PBL waste liquor activates the cement phases and improves the rate of hydration. The incorporation of PBL waste with OPC or LPC pastes enhances the w/c ratio for LPC more than OPC cement pastes and decreases the setting times (initial and final). So, it can be used as an accelerator. The combined water contents, bulk density and apparent porosity at all curing ages of hydration are improved and accordingly the compressive strength was increased, particularly at later stages of hydration (28 and 90 days). No new phases are detected by IR, but only increased intensities for the formed phases was observed by the addition of PBL waste than those of the blanks. The optimum PBL concentration is 2 wt. % because the higher concentration has adversely effect on all cement characteristics. The SEM images showed that the incorporation of the PBL waste with cement did not affect the OPC or LPC hydrates, but it only affected the physical state, shape or morphology and crystallinity of the formed hydrates. Also, the presence of PBL waste influences the morphology of the Ca (OH)₂ crystals and eventually has preferential efficiency with LPC pastes .

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