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Pulp White Liquor Waste as a Cement Admixture-Part I

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Abstract The pulp white liquor waste (PWL), a byproduct from paper-making, could be 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 0, 1, 2 and 3 wt. % PWL was gradually decreased, while the setting times (initial and final) were increased. So, it can be used as a retarder. The compressive strength increased slightly during the early ages of hydration (1 and 3 days), but sharply increased during the later ages (28 and 90 days), specially with those premixed with PWL. The combined water content and bulk density displayed the same trend as the compressive strength, whilst the apparent porosity decreased at all curing times up to 90 days. The IR spectra of cement pastes showed that the intensities of the different peaks of cement pastes with PWL are higher than those of the pure samples. The above results proved that 2 wt. % PWL is the optimum concentration.

Keywords: *PWL, OPC, LPC, combined water, bulk density, apparent porosity, Strength, FT-IR*

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1. Introduction

It is well known that the industrial wastes or byproducts either solid or liquid caused many environmental problems as air, soil or water pollution. So, the recent trend all over the world is to reuse these wastes in useful applications [1,2,3,4]. Although the nature and action mechanism of cement and/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 evidently improve the workability and also modify other properties of cement pastes, mortars and/or concrete. Furthermore, they enhance the performance of concrete structures [5,6,7,8].

Black and white liquors, waste products which are coming from Paper Industry (Figure 1), have attracted our attention due to their unique advantages because 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 [9]. Darweesh et al. [10] studied and used the black liquor waste as a cement admixture. The pulp white liquor (PWL), is a strong alkaline solution used in the first stage of the kraft process in which the lignin and hemicellulose are separated from the cellulose fiber in the kraft process for the production of pulp [2].

It is called white liquor due to its white opaque color. In the pulp and paper industry's Kraft pulping process, the so-called white liquor is charged together with wood chips, into the digester, at high pressure and temperatures up to 170°C. Within the digester, lignin from the wood is removed by action of the hydroxide (OH^-) and hydrosulfide (HS^-) ions producing a suspension of cellulose fibers. This suspension is the pulp. The white liquor that contains polysulfide ions is known to increase the process' yield. Pure sodium hydroxide solution (NaOH) is used in a number of situations in the pulping mill [11].

Uchikawa et al. [12] 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 white liquor constitutes a new and promising admixture.

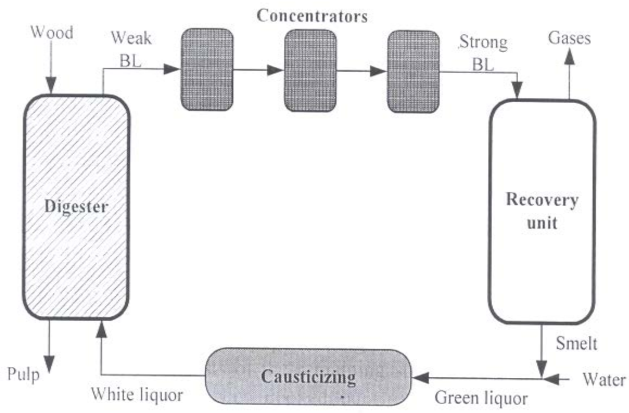

Figure 1. A schematic description of the pulping process

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 [13,14,15,16]. 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. [15] 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 [17,18]. 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. Experimental

2.1. Raw Materials

A waste of pulp white liquor (PWL) 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 cm^2/g were delivered from Helwan and Tourah Cement Companies, Egypt, respectively. The white liquor is mainly composed of NaOH and Na_2S in water. These are the active component in Kraft pulping [2]. It contains also minor amounts of sodium carbonate, Na_2CO_3; sodium sulfate, Na_2SO_4; sodium thiosulfate, $Na_2S_2O_3$; sodium chloride, NaCl, calcium carbonate, $CaCO_3$ and other salts as well as non-process elements. These additional components are considered inert in the Kraft process, except sodium carbonate that contributes to a lesser extent. The composition of typical white liquor is 3 M NaOH, 0.7 M Na_2S and 0.25 M Na_2CO_3 as shown in Table 1, while Table 2 shows the elemental analysis of the OPC and PLC cements.

Table 1. the composition of a typical white liquor

Oxides Materials	NaOH	Na_2S	Na_2CO_3
PWL, M	3	0.7	0.25

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

B. S. A cm^2/g	L.O.I	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Oxides Materials
3300	2.64	2.64	5.25	3.38	63.13	1.53	0.55	0.3	2.54	OPC
3100	6.44	16.10	4.03	3.80	60.10	1.24	0.65	0.26	1.44	LPC

2.2. Preparation and Methods

The PWL 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 cm^3), 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 thehe time of testing for bulk density, apparent porosity and compressive strength after 1, 3, 7, 28 and 90 days. The samples were denoted as P_0, P_1, P_2, P_3 for OPC and L0 L_0, L_1, L_2, L_3 for LPC.

The standard water of consistency (or mixing water) as well as setting times (initial and final) of the prepared cement pastes were directly determined by Vicat Apparatus [19,20]. The bulk density and apparent porosity [1] of the hardened cement pastes were calculated from the following equations:

$$B.\,D,\left(g/cm^3\right) = W_1/\left(W_1 - W_2\right)\times 1 \qquad (1)$$

$$A.\,P,\ \% = \left(W_1 - W_3\right)/\left(W_1 - W_2\right)\times 100 \qquad (2)$$

Where, B.D, A.P, W_1, W_2 and W_3 are the bulk density, apparent porosity, saturated, suspended and dry weights, respectively.

The compressive strength [21] 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:

$$Cs = \ L/SaKN/m^2 x\ 102/10.2 \qquad (3)$$

Where, Cs: Compressive strength (MPa), L: load (KN), Sa: surface area (cm^2).

The chemically-combined water content at each hydration age was also determined on the basis of ignition loss [1,22] as follows:

$$Wn,\% = W1 - W2/W2\ x100 \qquad (4)$$

Where, Wn, W1 and W2 are combined water content, weight of sample before and after ignition, respectively.

2.3. Phase Composition

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}.

3. Results & Discussion

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 0, 1, 2 and 3 wt. % PWL waste are plotted in Figure 2. Generally, the water of consistency gradually increased with PWL concentration up to 3 wt. % in both types of cements. Furthermore, the increase of water of consistency by using the same concentrations of PWL with LPC was slightly more than that with OPC. The 3 wt. % PWL waste increased the water of consistency from 28 to 31.67 wt. % with OPC and from 28.5 to 32.45 wt. % with LPC. So, the water of consistency was increased by 1.68-13.12 wt. % with OPC and by 4.11-13.85 wt. % with LPC compared with those of their blanks.

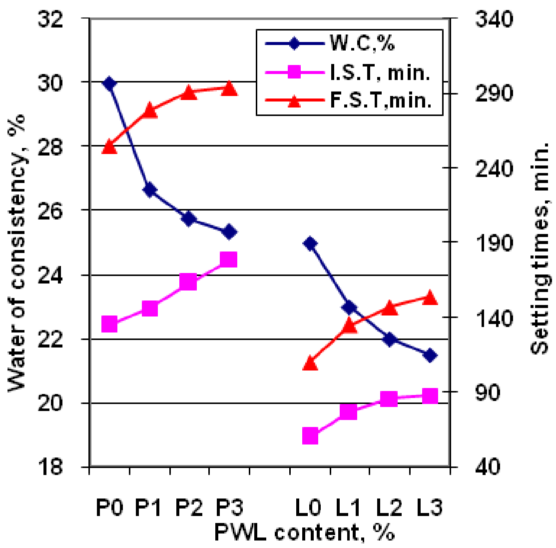

Figure 2. Water of consistency and setting times of the OPC and PLC cement pastes premixed with 0, 1, 2 and 3 wt. % PWL waste

On the other hand, both initial and final setting times with OPC or LPC pastes premixed with the PWL waste were gradually decreased. The 3 wt. % PWL 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 be used as a retarder for cement pastes [1,2,3,4].

3.2. Bulk Density and Apparent Porosity

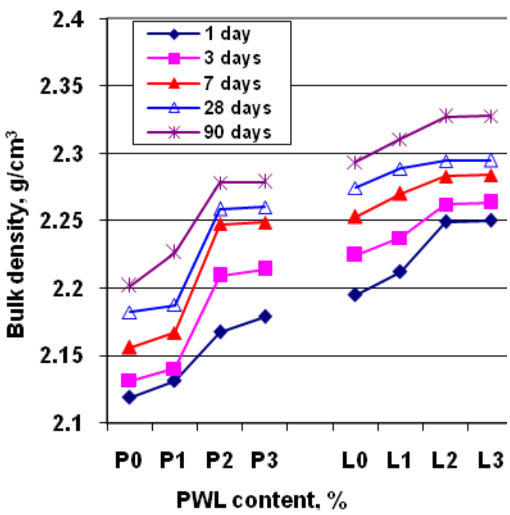

Figure 3. Bulk density of the OPC and PLCcement pastes premixed with 0, 1, 2 and 3 wt. % PWL waste cured up to 90 days

Figure 3 and Figure 4 show the bulk density and apparent porosity of the OPC and LPC cement pastes premixed with 0, 1, 2 and 3 wt. % PWL liquor waste, respectively. The bulk density was 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 system of the hardened cement pastes [1,14]. Moreover, the bulk density was further increased with PWL concentration up to 2 wt. % and be stable at 3%, whereas the apparent porosity decreased. This may be due to the activation of cement phases by the presence of NaOH in the waste liquor and subsequently the amount of hydration products were increased when compared with those of the blanks [2]. With further increase in PWL concentration as with 3 wt. %, both bulk density and apparent porosity were almost the same. Thereby, the 3 wt. % PWL concentration is not more effective than 2 wt. % and hence it must be avoided [2,3,4,5].

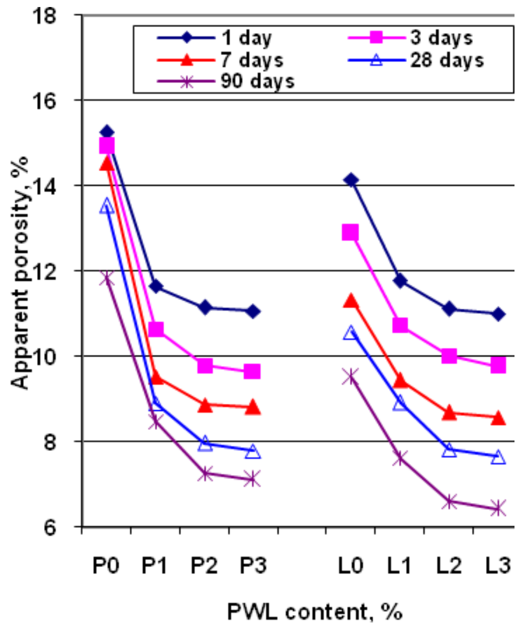

Figure 4. Apparent porosity of the OPC and PLC pastes premixed with 0, 1, 2 and 3 wt. % PWL waste cured up to 90 days

3.3. Combined Water Contents

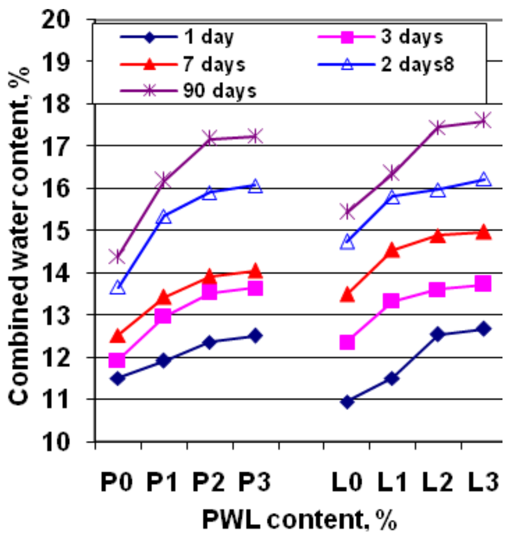

Figure 5. Combined water content of OPC and PLC pastes premixed with 0, 1, 2 and 3 % PWL waste cured up to 90 days

The combined water contents of the OPC and LPC cement pastes premixed with 0, 1, 2 and 3 wt. % PWL waste liquor are shown in Figure 5. The combined water contents of all cement pastes were 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 β-C_2S [1,16]. The combined water contents increased gradually by the incorporation of PWL liquor up to 2 wt. % with both OPC and LPC and then tended to be stable with 3 wt. % in case of Bulk and apparent porosity [1,15,23]. The combined water contents of cement pastes with LPC are slightly higher than with OPC. This may be due to that the active group in PWL waste (-OH) is more effective with LPC than with OPC pastes [2]. Because the 3 wt. % PWL is not more effective than 2 wt. %, it is not desirable. Also, the PWL waste displayed the same trend with both types of cements at all curing times, but slightly more with LPC pastes [2,14].

3.4. Compressive Strength

The compressive strength of OPC and LPC cement pastes premixed with 0, 1, 2 and 3 wt. % of PWL waste liquor is shown in Figure 6. 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. Hence, the bulk density increased and this was positively reflected on the compressive strength [1,16,24]. The decrease of the apparent porosity and increase of the bulk density resulted from further increase of the hydration products [4,5,23].

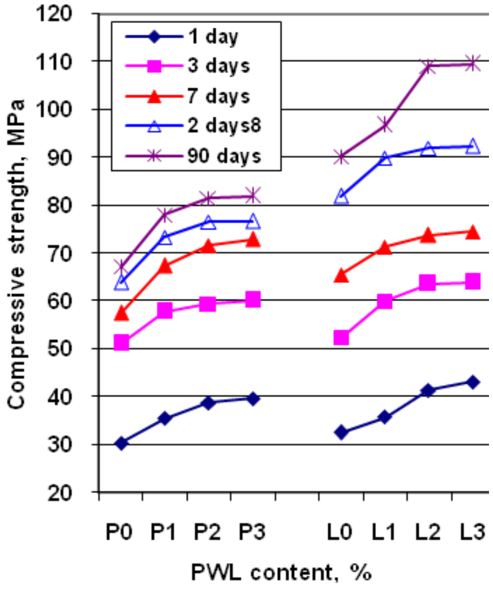

Figure 6. Compressive strength of OPC and PLC pastes premixed with 0, 1, 2 and 3 wt. % PWL waste cured up to 90 days

The higher compressive strength for both types of cement (OPC and LPC) compared with those of blank by increasing the PWL concentration up to 2 wt.% is mainly due to the high activation effect of the $-OH^-$ group present in the PWL particularly at later ages of hydration (28 and 90 days).

The addition of PWL waste to cement led to the formation of electrostatic repulsive forces between cement particles negatively charged by the adsorption of the liquor waste onto the cement surface which reduces the interparticle attraction between the cement particles leading to prevent the flocculation or agglomeration of cement. Accordingly a well-dispersed system is obtained [24,25,26]. Hence, the slight increase of w/c ratio and the dispersing effects (Figure 7) due to PWL waste addition helped to a large extent to improve and enhance the compressive strength [1,26,27]. With 3 wt. % PWL waste, the compressive strength was not affected and therefore the optimum concentration is 2 wt. %. Consequently, the higher concentration is unnecessary. Figure 8 demonstrates the dissociation and orientation of the admixture particles as soon as its addition to the mixing water while Figure 9 shows the adsorption of the admixture particles on the cement grains and its rearrangement to achieve the equilibrium.

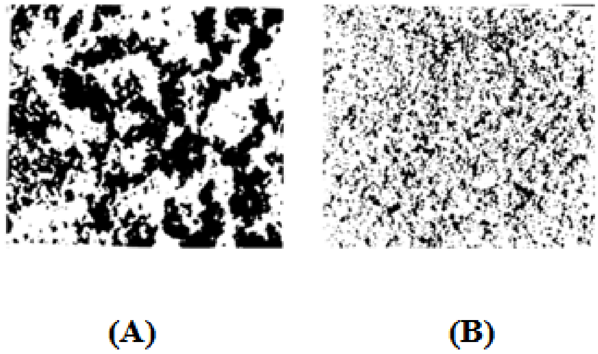

Figure 7. Dispersibility effect of admixtures, (A): In absence of admixture, (B): In presence of admixture)

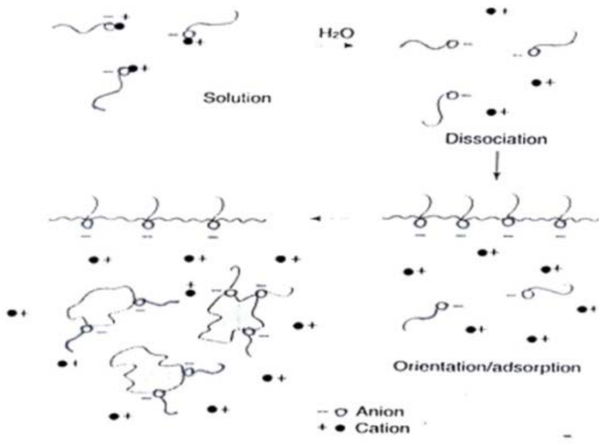

Figure 8. Surface reactivity and surfactant behaviour

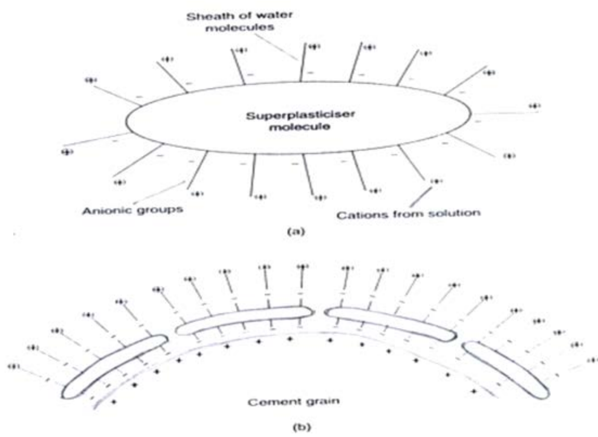

Figure 9. (a) Representation of an admixture molecule and (b) Mode of adsorption of admixture on cement grain

Also, the compressive strength values of OPC and LPC cement pastes are higher with the incorporation of PWL waste, where it is little more with LPC pastes than with OPC pastes. Therefore, the activation effect of the PWL liquor increased the rate of hydration which enhanced the cementing properties of the hardened cement pastes. This often has a positive action on the mechanical properties. It could then be recommended that the higher concentration of PWL waste (> 2 wt. %) is unfavorable with both types of cement. It is worth mentioning that the same trend achieved by using PWL waste was also achieved in a previous study [10] using the same concentration of black liquor waste (PBL) but with lower values, i.e. the PWL waste is more effective with both types of cements than PBL one.

3.5. IR Spectra

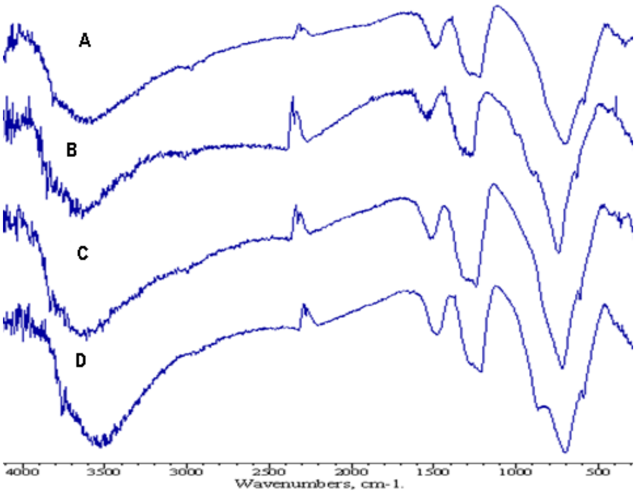

Figure 10. The FTIR spectra of OPC pastes cured up to 90 days (a), premixed with 1 wt. % PWL (b), 2 wt. % PWL (c) and 3 wt. % PWL (d)

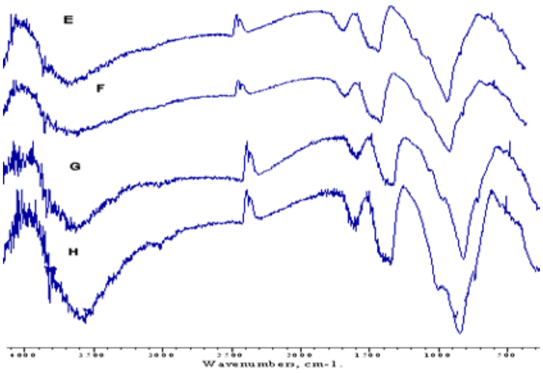

Figure 11. The FTIR spectra of LPC pastes cured up to 90 days (a), premixed with 1 % PWL (b), 2 wt. % PWL (c) and 3 wt. % PWL (d)

The FIR spectra of OPC (A-D) and LPC (E-H) cement pastes premixed with 0, 1, 2 and 3 wt. % of PWL waste are shown in Figure 10 and Figure 11, respectively. The sharp absorption band at 3644-3641 cm^{-1} is related to the free OH^- group coordinated to Ca^{+2}, i.e. Ca $(OH)_2$ or free lime. The intensity of the broad absorption band at 3450-3425 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 PWL liquor. The two absorption bands at 2960 and 2860 cm^{-1} are due to $-CH_2$ and $-CH_3$ from the residual organic mixture. The two absorption bands at 1645-1640 cm^{-1} and 1430-1422 cm^{-1} are related to the main silicate band involving Si-O stretching vibration bands of CSH, while the band at 1122-1112 cm^{-1} may be due to CAH. The intensity of the two absorption bands at 990-980 cm^{-1} and 874 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, the intensity of the absorption bands of Si-O, CAH, CO_3^{-2} and SO_4^{-2} are slightly higher with PWL waste cement pastes. The intensities of the main characteristic peaks were slightly improved with LPC than with OPC pastes.

4. Conclusion

The PWL liquor activates the cement phases and improves the rate of hydration. The incorporation of PWL waste with OPC and/or LPC pastes enhances the w/c ratio for LPC more than OPC cement pastes and increases the setting times (initial and final). So, it can be used as a retarder. The combined water contents, bulk density and apparent porosity at all curing ages of hydration are improved and gradually increased. As a result, 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 hydrates was observed by the addition of PWL waste than those of the blanks. The optimum PWL concentration is 2 % because the higher concentration (3 wt. %) has little or no further effect on all cement properties than 2 wt. %. The IR analysis showed the highly modified crystals of hydrates in presence of PWL. Moreover, the presence of PWL eventually has preferential efficiency with LPC pastes than with OPC pastes.

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