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Influence of date palm liquor on rheological behavior of cement-based mortars

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Abstract-The cost of superplasticizer is increasing day by day because of high demand, scarcity of raw materials. From this, the extensive research and development works towards exploring new ingredients are required for producing sustainable and environment friendly construction materials. Date palm liquor is one such material that can be used as a chemical admixture which is obtained with Kraft process from the date-palm wood. In the present investigation black liquor is added to fresh concrete in different dosages, the concrete is then tested for rheological behavior, workability and compressive strength.
From results it is shown that 1% replacement of water with black liquor increases the fresh properties of the concrete, 2% replacement of water with black pulp liquor increases the mechanical properties of the concrete and acts as a set retarder.

Keywords: *Date-palm wood, Black liquor, Cement, Rheological behavior, workability and compressive strength.*

1. Introduction

The world's most abundant renewable resource is biomass (wood and non-wood), of which the three main components are cellulose, hemicellulose, and lignin. In woody biomass, cellulose is the most abundant biopolymer, followed by lignin which accounts for 15 – 40 wt.% of wood [1,2].

Lignin is also the largest natural resource of aromatic compounds.[3,4] However, only 1 –2 % of the 50 – 70 million tons of lignin produced annually is used for the production of value-added products, implying that it is an underutilized material. [1,2], [4,5] Today, lignin is primarily used for energy generation through combustion in pulping processes. As such, it is highly advantageous to identify lignin based value-added products and to develop processes for their production.

Kraft process and soda process are the two major alkaline process used to convert the wood to pulp (Cardoso et al 2008) [6] and the solution obtained after the removal of the fiber product is called black liquor. This liquid consists of large amount of dissolved lignin [7]. There are different methods are available for extraction of lignin from black liquor but the conventional method like chemical pulping processes require large quantity of toxic materials and time requirement for the process is more. Nguyen Dang et al (2012) [8] has developed new simple and efficient method for extraction of lignin using non-toxic aluminum potassium sulfate dodecahydrate. Time requirement for extraction is also less in this method than the conventional method. Depending up on the type of raw material used and operational conditions of the pulping stages the chemical composition of the black liquor pulp will vary. This black liquor pulp consists of

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both organic and inorganic materials. This chemical composition has predominant role in determining its rheological and physical properties of liquor [9].

Darweesh et al (2013) [10] studied the effectiveness of black liquor pulp as admixture in cement paste made up of using Ordinary Portland Cement. Improvement in the workability, compaction and reduction in the setting time is observed in the concrete due to the addition of black liquor. Effectiveness of extracted lignin from black pulp in improving the workability and compressive strength was studied by Kamoun et al (2003) [11] and it is found that effectiveness of extracted lignin is comparable to those of a commercial LS-based plasticizer.

The main objective of this work is to verify the influence of lignin kraft on the rheological properties and workability of cement in the fresh state. The valorization of the lignin as admixture cement and concrete material is of major importance for our region. The lignin is extracted by the Kraft process from the date-palm wood waste of the TOLGA-Algeria region. This approach may help recover the huge quantities of date palm wood waste available in the south of the country. It also provides a low cost by-product, which can be widely used in the construction industry. The results obtained in this paper revealed that black liquor has similar performance compared to the commercially admixture. For that, all authors believe that the black liquor of date-palm wood has an important economic, ecological and scientific interest.

2. Experimental investigation

2.1 *Materials*

2.1.1 *Cement*

The cement used in this study is a CPJ-CEM II/A 42.5 type, supplied by GICA Company, Algeria. It is characterized by a Normal consistency of 26.7% and a finesse following Blaine's method (NA 231) [12] of 5820 cm^2/g. The mineral and chemical compositions of cement are given in the Table and 2, respectively.

Table 1. *The cement (CPJ-CEM II/A 42) mineral composition*

Mineral composition (%)	C3S	C2S	C3A	C4AF	Free CaO
CPJ-CEM II/A 42.5	53.90	21	7.11	11	≤ 1

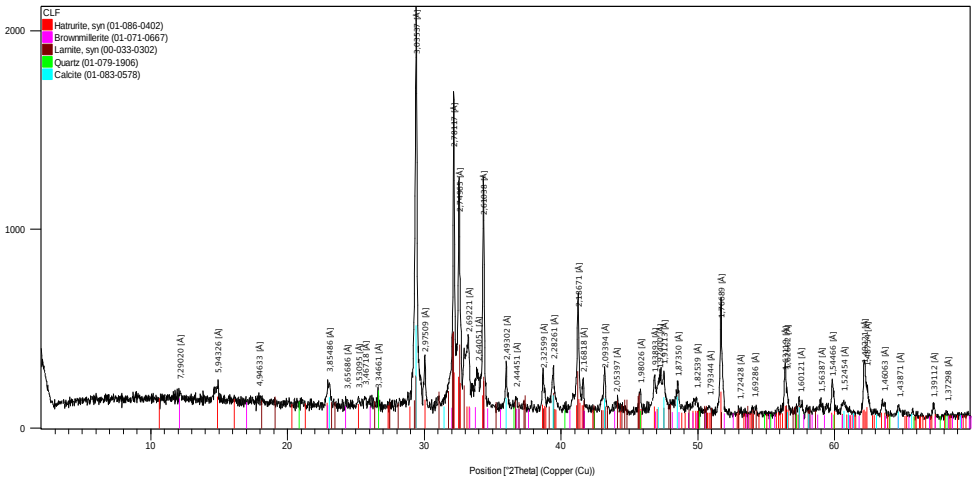

Figure1: *Diffractogram DRX of cement of cement* CPJ-CEM II/A 42.5

Table 2. *The cement (CPJ-CEM II/A 42.5) chemical composition*

	Constituents		Per cent by Weight (%).
1.	Silica (SiO_2)		22.88
2.	Iron Oxide (Fe_2O_3)		5.42
3.	Alumina (Al_2O_3)		4.24
4.	Calcium Oxide (CaO)		62.93
5.	Magnesium Oxide (MgO)		1.03
6.	Total Sulphur (SO_3)		1.22
7.	Alkalies	a) Sodium Oxide (Na_2O)	0.24
8.		b) Potassium Oxide (K_2O)	0.37
9.	Insoluble residue		0.78

10.	Loss on ignition	0.89

2.1.2 Black liquor

In this study, we extracted the lignin by the kraft process from the date-palm wood of the TOLGA-Algeria region. After extraction and sulfonation the Kraft lignin has been valued as superplasticizer in cement. Its physical characteristics and its rheological effect to the cement matrix have been studied.

3. Results and discussion

Table 3 shows the water Black liquor ratios adopted for the experimental study. Water cement ratio of 0.35 was selected to represent commonly used concrete, while the water cement ratio of 0.35 corresponds to higher strength concrete. Maximum amount of black liquor pulp added to the mix was limited to 1.75% because addition of higher amount of black liquor in concrete pulp leads to decrease in workability.

As the mixing sequence affect the properties of cement and concrete a uniform mixing sequence was adopted for preparing the mixes (Table 3). We set the W/C ratio to 0.35 and used five dosages of black liquor (0.5, 0.75,1, 1.25, 1.25 and 1.75%) by cement weight. Portland cement and aggregate were dry mixed first for two minutes and then water was added to the mix and mixed for 1 minute.

Table 3. *Mix proportion of cement past*

Cement (g)	410
Sand(g)	1240
Water (g)	143.5
Black liquor (%)	*0.5, 1, 1.5, 2 and 2.5*

3.1 Rheological measurements

3.1.1 Apparatus

The transient and steady state behaviours of the pastes were characterized using a stress-controlled shear rheometer (Brookfield HA DV II + Pro). In order to minimize sedimentation effects on rheological measurements, a co-axial cylinders geometry was chosen. In such a geometry, the tested material is subjected to an approximately uniform shear rate provided that the gap between the cylinders is sufficiently small compared to the diameter of the inner cylinder. On the other hand the gap has to be much greater than the larger heterogeneity length scale in the material in order to provide average measurements. In our case, the inner (mobile) cylinder was 25 mm diameter and outer (fixed) cylinder 29 mm. The gap was thus 2 mm, which satisfies the above-mentioned conditions in the case of the pastes considered here.

The temperature was fixed at 25 °C (to within 0.1 °C) thanks to a circulating liquid system. In order to prevent evaporation of the paste's water the measurement system was sealed.

3.1.2 *Transient behaviour*

Figure 2 shows the transient behaviour of the effective viscosity (stress divided by shear rate) as a function of time for different shear rates. Only results for the reference paste are shown here, but the results for the other tested pastes are similar. The dependence of the stress upon time of shearing is, as expected, related to the thixotropic character of the paste.

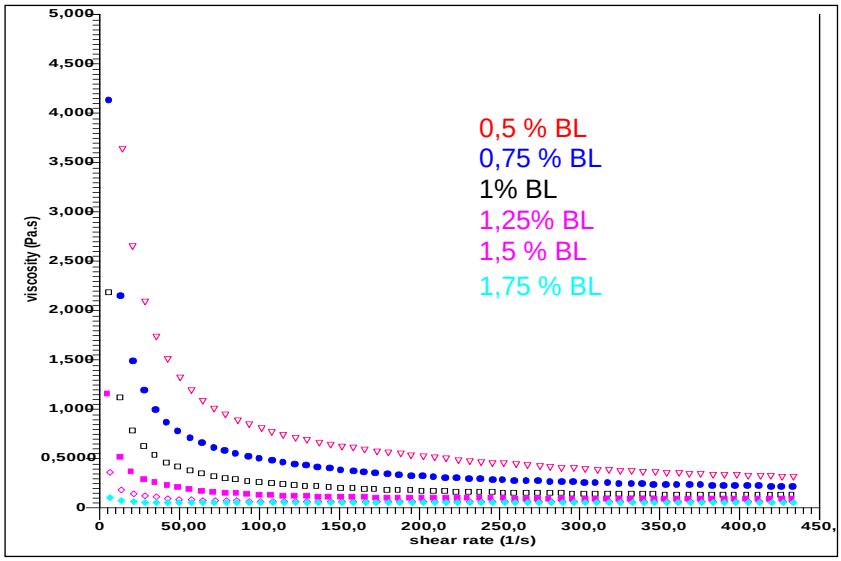

Figure 2. *Transient rheological behaviour of the reference paste for different shear rates*

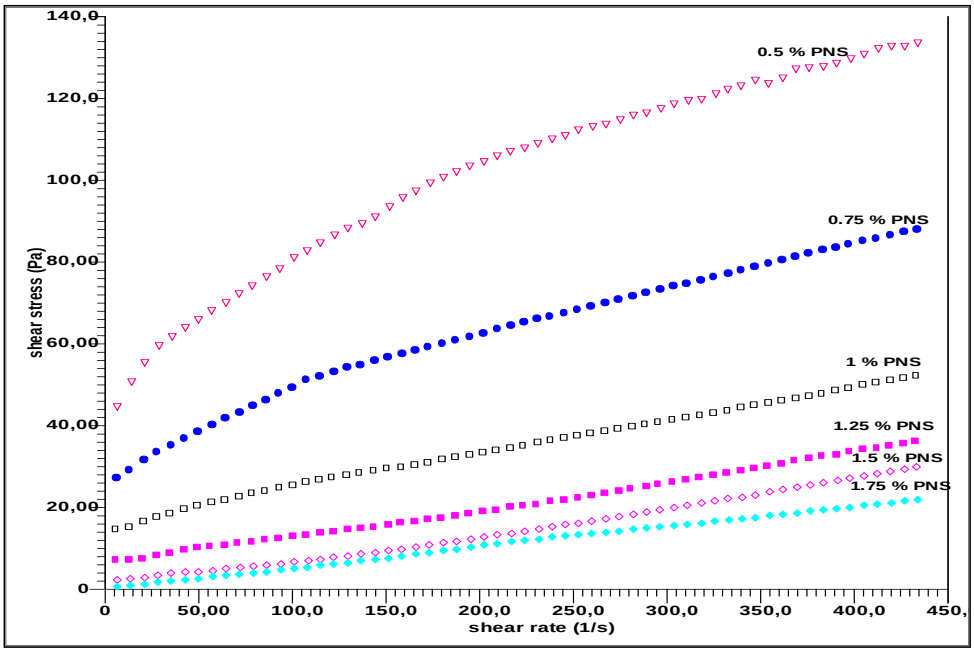

Figure 3. *Shear stress against shear rate in the shear thinning part of the rheograms.*

The curves of shear stress and viscosity according to shear rate for different dosages of black liquor (0.5, 0.75,1, 1.25, 1.25 and 1.75 wt% cement), are shown in Figure 3.

The results show that fluidity increases with an increase in dosage of black liquor up to the saturation dosage, who equal to (1.75%) for M2% BL. We also notice that at a certain dosage the dough flows without any effort (absence of the yield value) is the saturation point (1.75%) for M2% BL, causing the decrease of the flow threshold (threshold constraint). The higher the percentage of black liquor increases the viscosity of the dough decreases until it is constant (almost Newtonian flow); this is due to the dispersing effect of the black liquor, which adsorbs at the cement grain interface, creating repulsive forces between the particles, reducing or eliminating the adhesion between adjacent particles [13].

Black liquor acts positively and specifically on the rheological properties of cement pastes.

The intrinsic rheological parameters of the cement are determined by smoothing the experimental points of the rheograms. The smoothing model is that of Herschel-Bulkley (Equation 1).

$$\tau = \tau_0 + k\dot{\gamma}^n \quad (1)$$

Where τ is the shear stress in (Pa), $\dot{\gamma}$ is the shear strain rate (1/s), n is the power index, k is the consistency (Pa.s), and τ_0 is the yield stress (Pa).

Considering the case of the cement without the addition of the black liquor (BL), its rheogram and represented on the Figure 2. Smoothing with the Hershel-Bulkley model leads us to the following rheological parameters; τ_0 = -0.07 Pa and a viscosity of μ = 6.209 Pa.s.

Substitution of water by black liquor gives rheograms to a rheo-thickening behavior and the viscosity of the mortar decreases. The best smoothing is recorded in the formulation (M2% BL) show Figure 2. The parameters carried by the smoothing of the experimental points with the Hershek-Bulkly model are very good, the viscosity: μ = 0.01103 Pa.s and yield stress τ_0 = 2.494 Pa. This behavior is similar to that of self-compacting concretes with a fluidity index n> 1, which corresponds to rheo-thickening behavior which is generally reported in the literature [14-19].

Moreover, the addition of 1.75% BL with a W/C = 0.35 begets a better fluidity with the absence of segregation, the emulsifying aspect of the black liquor restrains the grains of cement, which separates the coarse grains by decreasing the friction between them.

The black liquor tested resulted in pastes with good fluidity, when the corresponding saturation dosages were used. It is concluded that the cement-black liquor combinations studied here are all compatible as far as the flow behavior is concerned.

4. Conclusion

The use of black liquor isolated from date palm wood has a very important scientist and economic interest. Black liquor is considered as a low cost admixture to increase the workability and compressive strength of concrete.

The results of this research show that black liquor produced from date palm trunk noticeably increases the workability of concrete with maximum performance at 1.75% water replacement by black liquor.

Effects of dosage of black liquor on the rheological properties of mortar and the rheological curves which have been studied to determine the saturation dosage. The yield stress and the plastic viscosity stress were dramatically decreased at dosage of 0.5–1.75 wt. %, compared with the sample without BL.

Both the Herschel-Bulkley and Bingham models fit the experimental data from the viscometer study satisfactorily. It is observed that the nature of flow in superplasticized paste varies slightly with the dosage of black liquor, as follows. At lower dosages, nonlinear shear thinning is generally observed; around the saturation dosage the response follows the Bingham model; and at higher dosages, there may be some shear thickening.

The yield stress values obtained with both the models have the same trend with respect to black liquor dosage, though the values from the Bingham model tend to be higher at smaller black liquor dosages. Even though shearthickening nature of paste is better represented through the Herschel-Bulkley model, the Bingham model represents the behavior of normal pastes well.

An increase in black liquor dosage leads to a decrease in the yield stress, plastic viscosity, and an increase in minislump spread, as long as the dosages are below the saturation point. Beyond the saturation dosage (1.75% of Water content), these parameters are practically constant.

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