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Black Liquor Waste Produced from Bagasse Kraft Pulping as an Admixture in Concrete

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ABSTRACT

The black liquor (BL) that obtained as a by-product of pulp and paper manufacturing process after digestion step, where the cellulose fibers have been removed from the bagasse, is one of such material that can be used as a chemical admixture. Annually, around two million tons of bagasse Kraft black liquor (BKBL) with 6:8wt% total dissolved solids (TDS) are produced in Egypt. The discharge of black liquor to water resources causes serious of environmental issues in contrast with adding it to concrete as an admixture has a positive impact on environment beside economy. Adding of BL to concrete improves its properties such as workability, compressive strength and setting time (initial and final). In this study BKBL is added to fresh concrete at different concentrations (0, 1, 2, 3, 4%), the concrete is then tested for bulk density, apparent porosity, setting time, workability (slump test), and the compressive strength. The results showed that mixing of concrete with BKBL up to 2 wt% has a positive effect on compressive. The initial and final setting times were increased by adding black liquor, so it can be used as a retarder. Adding of 2 wt% of BKBL is the recommended value that gives optimum improved results. These results open the door for utilization of black liquor from Qena Paper Industry Company, Quse, Egypt as an admixture to improve concrete properties.

1. Introduction

For a long time, wood, rice straw and sugarcane bagasse (waste material), were used as feed stock for pulp and paper industry. Kraft process is the most common chemical pulping process, accounting for around 80% of world pulp production [1]. In this operation, the cellulosic materials, wood, rice straw and bagasse, and various chemicals (e.g., NaOH and Na_2S), collectively known as white liquor, are cooked at high temperature and pressure in a digester to produce pulp and a complex residual filtrate, referred to as black liquor due to its dark color, Figure 1. During the digester, the hydroxide (OH^-) and hydrosulfide (HS^-) ions dissolves lignin to produce colloid cellulosic fiber (pulp). Other situations use pure NaOH for digestion step where; dissolving of lignin by hydroxide ions (OH^-) that called soda process pulping.

Nowadays in Egypt, the sugarcane bagasse represents the main source of lignocellulosic materials for pulp and paper manufacturing and produced huge amount of black liquor waste, around two million tons 6:8wt% TDS per year. The Quena pulp and paper mill, Qous city - Quena governorate, produces 3500 tons/day while; the Edfu pulp and paper mill, Edfu city - Aswan governorate, produces 1500 tons/day black liquor as a waste form bagasse pulping process. The continuous discharge of pulp black liquor waste to the land and other discharging channels will cause serious environmental issues.

Black liquor is a mixture of inorganic chemicals and a large amount of organic chemicals, chiefly lignin. For this process to be cost-effective, the cooking chemicals that react with the raw material and subsequently contribute to the production of black liquor must be recovered. In order to regenerate these chemicals, black liquor is subjected to several environmentally deleterious and energy-intensive treatments such as evaporation and burning. Rising energy costs and strict environmental regulations dictate that black liquor must be combusted at the highest possible solids concentration; however the ultimate concentration of black liquor is limited in practice by rheological considerations, since black liquor exhibits an exponential increase in viscosity as its solids content raises [2]. Utilization of the produced black liquor is still not efficient where; a portion of the annually produced black liquor is treated for chemicals recovery [3]. Otherwise, the chemical recovery from black liquor produced from pulping of rice straw is very difficult due to its high silica content that causes a series of problems; scaling, corrosion, act. [4,5]. So try of using pulp black liquor wastes as a viable save material can reduce environmental issues and improve the process economy.

Similar to those of most of the paper mills worldwide, other utilization of black liquor as a heat source by burring it in waste heat boilers to generate steam required for the different process sectors but, the net energy produced is limited where; it must be concentrated before the burring. A large amount of the annually produced black liquor (from rice straw) is mainly discharged as a waste that causing environmental problems. One of solutions to the process becomes cost effective is the utilization of this liquor in other applications.

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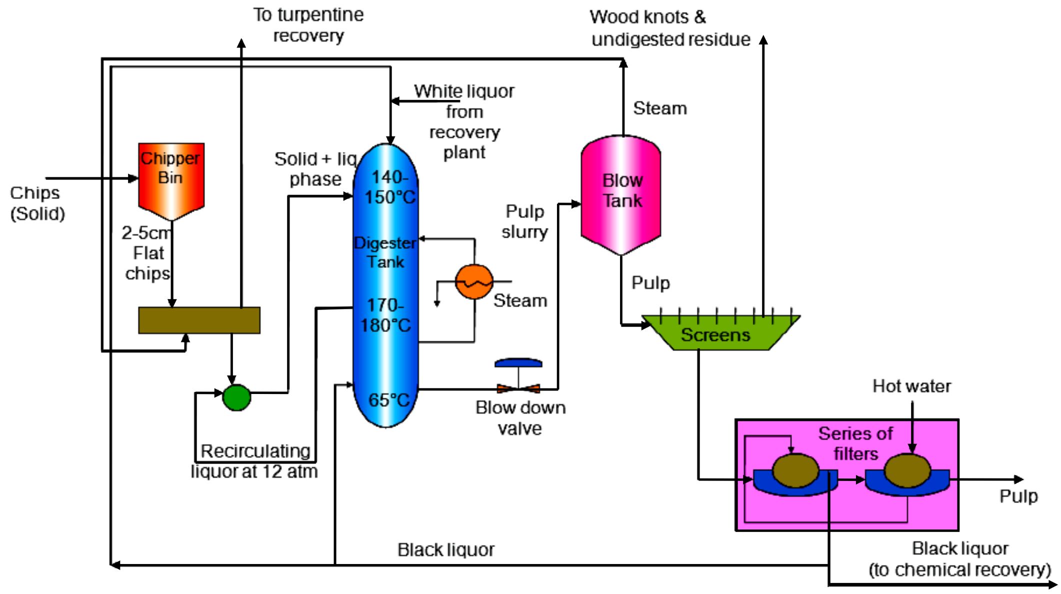

Figure 1: General flow sheet of chemical pulping process.

On other side, the concrete as cement materials is one of the most consumed materials over the world. It has been used in nearly all types of construction such as buildings, highways, canal and tunnel lining; support of underground mine roadways, bridges and dams, etc. Concrete is a composite material consists of aggregates in different size distribution and filler materials embedded in a hard matrix material (the cement or binder) that fills the voids between the aggregate particles and glues them together. Some of cement admixtures are used in minor quantities that effect on the physic-mechanical properties and its performance in different applications. Admixtures are defined as materials other than fine and coarse aggregate, water, fiber and cement, which are added into concrete batch immediately during or before mixing. The widespread use of admixture is mainly due to the many benefits made possible by their application and thus become an essential component of modern concrete. The chemical admixture such as water soluble polymers, liquid resins and monomers can effect on some of cement characteristics, strength, durability, workability, reduction of water requirements, control the setting and accelerating of hardening [6]. The common water soluble admixtures employed as cement modifiers are cellulose derivatives including methyl-, carboxymethyl-, hydroxyethyl-cellulose, polyethylene oxide, polyvinyl alcohol, polyacrylamide, and act. [7].

Generally, for all sorts of industrial raw material, creation of safe useful products from the waste materials has a double benefit, not only increases income for the industry but also a solution to the pollution problem. Some of published articles reported that adding of some organic admixtures make physical effect, which improve the bonds between particles as well as effects explicitly on the chemical process of hydration, especially on the crystal growth [8]. Some reports describe the use of alkaline black liquor as a workability aid for mortar and concrete, and show that alkali black liquor has a positive effect for concrete durability in same time does not have any negative effect on steel corrosion [9].

Other research on utilization of wood pulping black liquor as an admixture in concrete where, two properties of concrete were studied, compressive strength and setting time has been studied. Design mixes of M20, M25 and M30 were prepared with a water cement ratio 0.42. In this article they concluded that PBL is considered as a cost effective admixture to increase the workability and retard setting time of concrete. The PBL waste activates the cement phase and improves the rate of hydration [10]. In other one the effect of addition black liquor on concrete properties like workability, split tensile strength and compressive strength has been investigated [11]. The values of compressive strength and tensile strength increased up to certain percentage of pulp black liquor. The maximum improved results were found at 1.5% black liquor. The addition of PBL waste to cement led to the formation of electrostatic repulsive forces between cement particles and in turn the adsorption of the liquor waste onto the cement surface which reduces the inter particle attraction between the cement particles and helps to enhance the compressive strength [12].

Thus utilization of black liquor as a concrete admixture is an economic added value. The confirmed achievements in this field attracted the attention of researchers to apply a large number of industrial organic wastes as cement admixtures while, according to my belief, there is no published information on the use of black liquid produced from bagasse Kraft pulping as admixture for concrete. So, our study aims to investigate possibility of using bagasse Kraft black liquor, produced as a byproduct from Quena paper mills (BKBL) as an admixture enhances the physico-mechanical properties of concrete, which represents an easy and economically solution to environmental problem.

2. Raw Materials and Methods

2.1. Raw Materials:

A number of experiments had to be performed on concrete containing black liquor in order to confirm reliability of the improved concrete according to Egyptian Standards. Furthermore, experiments were carried out on cement paste made by combining cement with water and black liquor to verify the cement's initial and final setting times. This section will cover all of the components used to prepare concrete samples (cement, fine aggregate, coarse aggregate, water, and additive).

Bagasse Kraft black liquor: The pulp black liquor is a waste material produced from paper industry which has high solubility and it is easily available with no cost; due to these characteristics, we are attempting to employ it as an additive in concrete. The black liquor used in this study was Egyptian black liquor resulting from Kraft pulping of bagasse (BKBL), it was provide from, Quena Paper Industry Company, Kous, Quena, Egypt. The black liquor was taken after separation unit at 7.6wt% dry solid content, it used without any treatment or concentration. Table 1 represents the average chemical composition of bagasse in Egypt, while both physical and chemical properties of black liquor used are presented in Table 2. These analysis was done in laboratories of Quena company and was found in attach with published data [13 & 14].

Table 1: Average chemical composition of bagasse.

Typical Comp. (wt.%)	Cellulose	Hemicellulose	Lignin	Extractives	Ash
	44.08	23.39	20.90	8.98	2.65
Elemental Comp. (wt.%)	C	H	O	N	Ash
	47.00	6.50	43.85	--	2.65

Table 2: Average Constituents of BKBL [Quena Lab.]

Particulars	Value (wt.%)
A. Elemental analysis	
Total Carbon, C	33.80
Total Oxygen, O	41.50
Total Sodium, Na	19.3
Total Hydrogen, H	3.60
Total Sulfur, S	0.70
Total Nitrogen, N	0.20
Total Potassium, K	0.10
Total Chlorine, Cl	0.07
Silica, Si	0.73
Total	100
B. Chemical Properties	
Total Solids (wt.%)	7.6
PH	12.5
Organic (wt.%)	79.3
Inorganic (wt.%)	20.7
Lignin (wt.%)	25.9
Residual Active Alkali RAA, As Na_2O, g/L	4.3
Total Alkali TA, As Na_2O, g/L	15.5
Sp.Gr.	1.027
Total Suspended Solids, mg/L	30.0

Cement: when it mixed with water, has the important property of setting or hardening, which serves to fill voids and give concrete density. All experiments were conducted with Ordinary Portland Cement-Grade 53, which is known for its outstanding quality and durability. The approximate chemical composition of the Ordinary Portland Cement (wt %) is: 2.11 SiO_2, 62.45 CaO, 5.41 Al_2O_3, 3.62 Fe_2O_3, 1.11 MgO, 0.55 Na_2O, 0.30 K_2O, 3.17 SO_3^{--}, 0.04 Cl^- and 2.81 L.O.I.

Fine aggregate: Sand from a single source was used as the fine aggregate throughout the study. To comply with the Egyptian Code of Practice, the particle size distribution of fine aggregate was assessed using conventional sieve analysis where the fineness modulus was 2.44.

Coarse aggregate: The coarse aggregate used in all experiments was naturally uneven and partly rounded at the edge, with size ranging from 10 to 20 mm. A sieve analysis was done to determine the particle size distribution for samples and used to satisfy the requirements of Egyptian Code, the fineness modulus was found to be 1.71.

Water: it is the important component, which, combined with cement, makes a paste that holds the aggregate together. All samples were casted using potable water from the laboratory line, which is of acceptable quality and meets the standard for concrete manufacturing.

2.2. Methodology:

To evaluate the effective of addition black liquor as an admixture for concrete, different design mixes were casted with different dosages of black liquor such as 0,1,2,3 and 4%. Design mix of M20 was prepared with a water cement ratio 0.47. The mixing proportions of the concrete components which follow the Egyptian standard are presented in Table 3. In order to grudge the effect of additives, set of physical and mechanical properties were measured at different BL dosage namely, bulk density, apparent porosity, slump value, initial setting time, final setting time and the compressive strength. The presented values are an average of two measuring values for each experiment.

Table 1: Mix design (concrete constituents) for M20 grad.

Constituent	Value
Cement (kg/m^3)	360
Fine aggregate (kg/m^3)	1410
Coarse aggregate (kg/m^3)	705
Water/cement	0.47
Black liquor dosage (wt.%)	0, 1, 2, 3, 4

3. Results and Discussion

3.1. Bulk density and apparent porosity

Figures 2 and 3 show the bulk density and apparent porosity of concrete premixed with 0, 1, 2, 3, and 4wt% of black liquor waste, respectively. Each measurement was an average of three similar cubes. The bulk density increased as the curing time progressed, while the apparent porosity decreased. This is may be explained due to the gradual and continuous deposition of produced hydration products in pore structure of the hardened cement pastes [15, 16]. Furthermore, increasing the BKBL content up to 2wt% enhances the bulk density while it decreases the apparent porosity. This could be ascribed to the presence of Na(OH) and Na_2S in the waste liquor activating and improving the hydration process of cement phases, resulting in an increase in the amount of hydration products compared to the blanks [17].

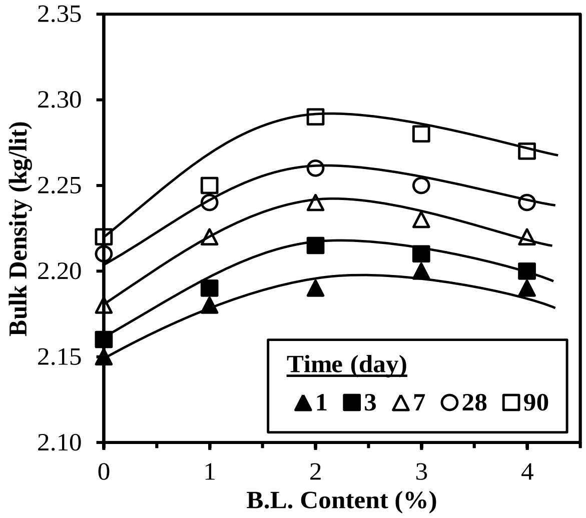

Figure 2: Bulk density of concrete for different BKBL content cured up to 90 days.

The bulk density was somewhat lowered and the apparent porosity increased as the BKBL content was increased over 2wt%. As a result, more addition of black liquor are undesirable and should be avoided where, a ratio of 2wt% was the optimum value. At 2wt% black liquor content, that percentage increase in bulk density was 1.86, 2.55, 2.75, 2.80 and 3.15 after 1, 3, 7, 28 and 90 cured days respectively, while percent reduction in apparent porosity was 22.8, 25.3, 30.96, 29.58 and 27.78 for the same cured days respectively. Same effects were observed in previous work when PBL was applied as a cement admixture [16].

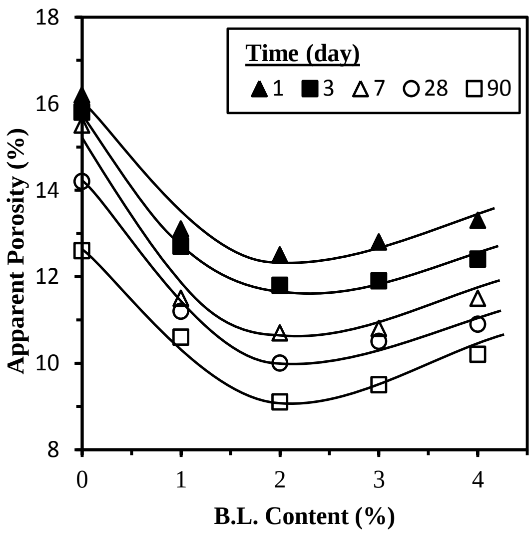

Figure 3: Apparent porosity of concrete for different BKBL content cured up to 90 days.

3.2. Slump Test.

The slump test was performed to determine the workability of fresh concrete. After the mixing procedure was completed, the fresh test sample was removed from the pan mixer and poured into a metal slump cone with a bottom diameter of 200 mm, a top diameter of 100 mm, and a height of 300 mm. As required by the ECP, the procedures were carried out in accordance with Egyptian Standards (1658/1989). To ensure optimum concrete compaction on the working site, the minimum allowable slump limit is 70 mm. Figure 4 shows the effect of the addition of BKBL on concrete slump at 0.47 w/c ratio.

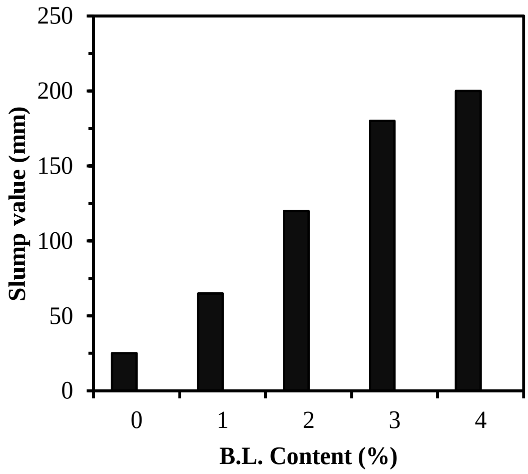

Figure 4: Effect of addition BKBL on slump value.

The slump value for the blank sample (0wt% BKBL) was 25 mm, indicating that this ratio is not suitable for the components in this combination and by adding black liquor, the slump value increased. It reached to 65, 120, 180 and 200mm for 1, 2, 3 and 4wt% BKBL as an admixture respectively. This is due to lignin, which is the cementing material that bonds the cellulose fibers in the cane bagasse, is one of the main constituents of the black liquid, and therefore its adhesive nature, which enhances cohesion and agglomeration of the mixture.

3.3. Setting Time

The initial and final setting time of concrete mixed with BKBL at different dosage up to 4wt% was measured. According to national guidelines, the initial setting time of Portland cement should not be less than 45 min, and the final setting time should not be more than 6.5 h. The obtained results indicated that initial setting time of pastes mixed with black liquor at various dosages (0:4wt. percent) was greater than the minimum limits, while the final setting time was less than the maximum limits; additionally, times increased as the BKBL content in the paste increased, Figure 5. This could be due to the fact that black liquor includes carbohydrates that serve as a retarder.

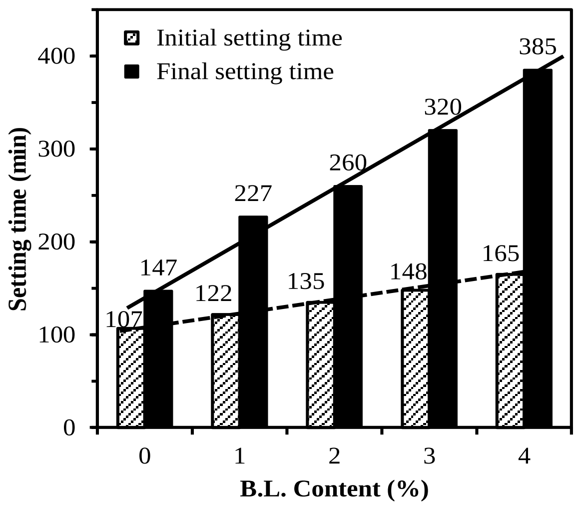

Figure 5: Effect of addition BKBL on concrete setting times.

3.4. Compressive Strength

Compressive strength is the ability to carry loads on the surface without any cracking or deformation. This test can simply judge the concrete strength in psi as well as its quality. The concrete strength depends on the specific compressive strength of its components (cement, sand, and aggregates), the quality of the materials used, curing procedures, water-cement ratio, air entrainment mixture ratio and many other factors.

A calibrated hydraulic press was used to measure the compressive strength of 20cm side length concrete cubic specimens in laboratory of ASEC Company for mining, Qena sector. The loading rate that used during compression tests was 1mm/min. while specimens ware tested for 1, 3, 7, 28 and 90 curing times.

Figure 6 depicts the effect of applying BKBL with different dosages on concrete compressive strength. It has the same behavior similar to bulk density for all hardening times; addition of BKBL has a positive effect on both properties up to 2wt%, and then has a bad effect with adding more liquor. Generally, the compressive strength growth with curing time up to 90 days for all BKBL content, it increases from 20.5 to 43.0 MPa at 1 wt.% liquor content for one and 90 days curing time respectively, while it increases from 22.5 to 45.5 MPa at at 3wt% liquor content for the same curing times. This is due to the continuous generation of hydration products, which deposit within the mixture's pore structure. As a result, apparent porosity decreased over time and sample compactness improved up to 2wt%, which had a favorable impact on compressive strength. The addition of BKBL waste to the cement mixture caused the creation of electrostatic repulsive interactions between negatively charged cement particles, which reduced interparticle attraction and prevented cement flocculation or agglomeration, resulting in a well distributed system [18]. The compressive strength was considerably affected until 2wt% BKBL concentration, which is consistent with porosity changes with additive content.

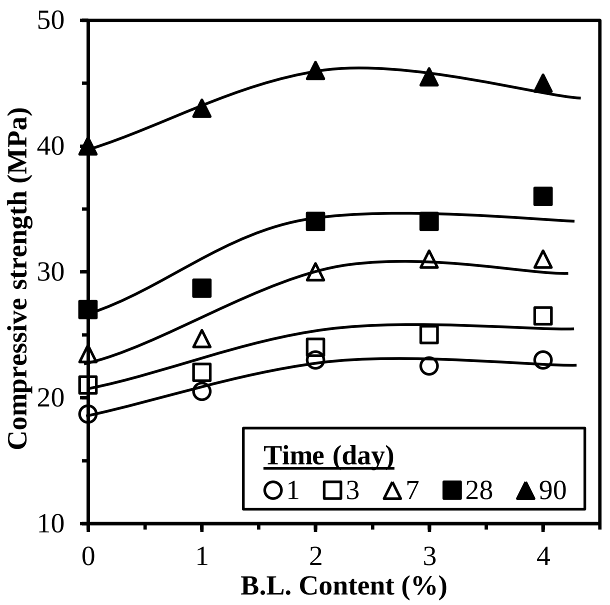

Figure 6: Effect of addition BKBL on concrete compressive strength after different curing time

4. Conclusion

One of the wastes that pose a significant environmental risk is black liquor. Quena pulp and paper mill produces 3500 tons/day black liquor as a waste form bagasse pulping process (6:8% TDS). The impacts of BKBL waste as a low-cost additive in concrete were investigated including its effect on: bulk density, apparent porosity, workability, setting time, and compressive strength. BKBL was added at different concentrations (0, 1, 2, 3, & 4 wt%), and the results showed that liquor waste activates the cement phases and improves the rate of hydration, hence improving the cementing characteristics of the hardened concrete. This has a positive effect on the mechanical properties, increasing workability and delaying setting time, which may be advantageous in situations where the concrete must be cast over a longer period of time. The highest bulk density as well as lowest apparent porosity was found at 2wt% BKBL concentration. The bulk density was 2.19, 2.21, 2.24, 2.26 and 2.29 kg/lit in contrast with apparent porosity that was 12.5, 11.8, 10.7, 10.0 and 9.1% for the 2wt% liquor content after 1, 3, 7, 28 and 90 days curing ages respectively. Finally, it was confirmed that using BKBL as a partial replacement for mixing water enhanced workability and compressive strength up to 2wt% liquor content while the setting time improved up to 4wt% liquor content.

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