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Fly Ash as Environmentally Friendly in Tannery Beam House Processes

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Abstract*—Over the years and till now, the beam house processes in tanneries, which include soaking, liming-unhairing and reliming causes a remarkable increase in BOD, COD and TSS. Although replacement and substitution of materials such as enzymatic unhairing, hair saving processes trials that were introduced, yet they practically require a very robust control, which is difficult to realize for mass production. Recently, Khartoum Refinery is faced with refining heavy crude oil, a case which needs a delay cooking unit that produces about 700 tons of coke per day. Successful endeavors using such coke for electricity generation has been made in practice at Garri Power Station. The emission of CO_2 can be managed and controlled, but there are a lot of fly ash accompanying this utilization. Physical and chemical properties of that fly ash show that the pH is alkaline (11-12). Its particle size and its effect on environment made it a suitable candidate as a beam house sharpening and unhairing agent. Experiments on these beam house processes were made for sheep skins from raw through crust and finishing. The results gave a very good physical properties including tensile strength, resistance, load at burst and gain crack. In this paper, it is recommended to apply such fly ash as a substitute of lime and part of sodium sulphide in soaking, liming-unhairing and reliming.

***Keywords*—Fly Ash, Soaking, Liming, Unhairing, Environmental Protection.**

I. INTRODUCTION

This paper describes the use of the produced fly ash from Garri Power Station Plant in the beam house processes in tannery. Fly ash is one of the by-products that are generated from the coke burning process. In Garri Power Station Plant, massive quantities of fly ash are being generated (1542 cubic meters per month). This large quantity of fly ash has created enormous problems.

Fly ash particles are generally spherical in shape and range in size from 2µm up to 10µm. They consist mostly of silicon oxide (SiO_2), aluminum oxide (AlO_3), ferric oxide (Fe_2O_3), calcium oxide (CaO) and carbon. The properties of fly ash vary from one sample to the next. Generally, fly ash is utilized in many sectors such as construction materials, e.g. as a partial replacement of cement in concrete and mortar applications, bricks manufacturing, road making, and to increase pH of the soil. Applications of fly ash depend on the quality of the fly ash (FA) used [8].

The process of converting raw hides and skins into leather is called tanning. There are two types of tanning operations; chrome and vegetable tanning. Tanning involves a complex combination of mechanical and chemical processes. The operations fall in three stages, which are pre-tanning, tanning and post-tanning. Pre-tanning processes are soaking, unhairing, reliming, fleshing, deliming, bating and pickling (also known as beam house processes) followed by tanning process and post tanning, such as shaving, retannage, neutralization, dyeing, fat liquoring and finishing [7].

Using of the fly ash from Garri Station in leather industry had many objectives, e.g. protection of the environment, mitigation of beam house pollution load, importing substitution and reduction of leather processing cost.

II. EXPERMENTAL WORK

A. Materials and Tools

The experiments and the analysis of samples of materials during this research project have been carried out in several locations, which are Leather Industry Incubator of the College of Engineering Industries and Technologies at Sudan University of Science and Technology and the Institute of Environmental Research and Natural Resources at the National Centre for Research.

Experiments carried out through this research included several materials, tools, apparatus and machineries. Materials were such as fly ash from Garri Power Station Plant, dry salted sheep skins, the necessary chemicals (e.g. Calcium Hydroxide, Sodium Sulfide, Sodium Bichromate, Ammonium Sulphate, etc.) which are required

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for the operations starting from soaking up to finishing. Tools and machineries are such as pilot plant drum, weighing balance, pH paper, fleshing machine, shaving machine.

B. Methodology

Nine pieces of dry salted sheep skins were brought from a warehouse. Then, one piece (the control sample) was treated using the standard procedure and materials. The rest eight pieces were treated in the soaking, unhairing, liming and reliming using fly ash from Garri Station.

The nine pieces were fleshed, de-limed, bating, pickled, and tanned up to finishing with the normal tanning procedure. The experiments were treated with different portion of fly ash as follows:

Control Sample: 1% Na_2S was used to raise the pH in the main soaking, then 4% Na_2S + 5% $Ca(OH)_2$ was used for the unhairing and then it was relimed with 2% $Ca(OH)_2$.

Treatment No. 1: The fly ash was used to raise the pH in the main soaking, then (10 % fly ash only) was used instead of the Na_2S+Ca $(OH)_2$ for the unhairing process, and then it was relimed with 2%fly ash.

Treatment No. 2 The fly ash was used to raise the pH in the main soaking, then (15%fly ash only) was used instead of the Na_2S+Ca $(OH)_2$ for the unhairing process, , and then it was relimed with 2%fly ash.

Treatment No. 3 The fly ash was used to raise the pH in the main soaking then treated with (1.0% NaOH +10%fly ash) was used for the unhairing, , and then it was relimed with 2%fly ash.

Treatment No.4 The fly ash was used to raise the pH in the main soaking then treated with (0.5%Na_2S+0.5%NaOH +10% fly ash) was used for the unhairing, , and then it was relimed with 2%fly ash.

Treatment No. 5 The fly ash was used to raise the pH in the main soaking then treated with (1%Na_2S+0.5%Na OH+10% fly ash) was used for the unhairing, and then it was relimed with 2%fly ash.

Treatment No. 6 The fly ash was used to raise the pH in the main soaking then treated with (2%Na_2S+10% fly ash) was used for the unhairing, and then it was relimed with 2%fly ash.

Treatment No. 7 The fly ash was used to raise the pH in the main soaking then treated with (4%Na_2S+5% fly ash) was used for the unhairing, and then it was relimed with 2%fly ash.

Treatment No. 8 The last piece was treated by hair saving process, using the normal paint formula with the exception that lime and kaolin were replaced by the fly ash (150 parts Na_2S + 300 part fly ash +0.5% wetting agent + 1.0 liter water).

The degree of unhairing was assessed in each treatment and then the unhaired skins were fleshed, de-limed, pickled, tanned, shaved, re-tanned and finished in the normal procedure. After that, the physical and chemical analysis was carried for each skin. Also the liquor of the control sample treatment and the most successful treatment (No. 7) were analyzed for the BOD and the COD.

III. RESULTS AND DISCUSSIONS

The six samples of fly ash were brought from Garri Power Station Plant and analyzed at laboratory of the Institute of Environmental Research and Natural Resources.

TABLE. I: ANALYSIS OF DIFFERENT SAMPLES OF FLY-ASH *

sample	Na_2O%	K_2O%	SiO_2%	Ca O%	Fe_2O_3%	SO_4-S mg/kg
1	2.938	1.344	78.95	6.483	0.028	52.80
2	12.488	7.457	39.30	10.910	0.065	126.72
3	3.673	1.897	47.25	7.580	0.051	100.32
4	3.305	1.643	65.48	4.923	0.033	58.08
5	4.040	1.517	39.55	11.994	0.084	63.36
6	3.305	0.505	69.65	2.299	0.045	73.92
Average	4.986	2.393	56.697	7.365	0.051	79.2

* Institute of Engineering Research and Materials Technology (IERMT) at the National Centre for Research.

Note: Sample 2 was used in main soaking, unhairing and reliming.

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TABLE II: PH AND THE SOLUBILITY OF THE FLY ASH USED IN THE UNHAIRING COMPARED TO THE HYDRATED LIME

Sample	pH	Solubility (g/100g)
Hydrated Lime	11	1.33
Fly Ash	11.5	2.8

TABLE. III: DEGREE OF UNHAIRING (FOR SAMPLES OF EXPERIMENT 1 THROUGH 8)

Treatment	Degree of Unhairing
Control	Excellent
1	Good + slight mechanical action
2	Good + slight mechanical action
3	Good + slight mechanical action
4	Very good + very slight mechanical action
5	Very good + very slight mechanical action
6	Very good + very slight mechanical action
7	Excellent
8	Excellent

TABLE. IV: THE AVERAGE VALUE OF TENSILE STRENGTH (FOR SAMPLES OF EXPERIMENT 1 THROUGH 8)**

Sample	Tensile Strength (perpendicular) kg/cm^2	Tensile Strength (parallel) kg/cm^2	Average Tensile Strength kg/cm^2
Control	132.35	219.1	175.73
1	142.75	219.85	181.3
2	235.55	340	287.78
3	182.5	155.3	168.9
4	131.8	307.75	219.78
5	222.4	318.45	270.43
6	271.05	333.5	275.28
7	192.3	300.7	246.5
8	279.57	152.1	215.84

**Leather Industry Incubator, College of Engineering Industries and Technologies at Sudan University of Science and Technology (SUST).

TABLE. V: THE AVERAGE VALUE OF ELONGATION (FOR SAMPLES OF EXPERIMENT 1 THROUGH 8)***

Sample	Elongation%(perpendicular)	Elongation%(parallel)	Average Elongation%
Control	70	68	69
1	98	87	92.5
2	107	61.2	84.1
3	73	67	70
4	82	58	70
5	88	86	83

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6	96	51	73.5
7	117	68	92.5
8	56	63	59.5

*** Leather Industry Incubator, College of Engineering Industries and Technologies at Sudan University of Science and Technology

TABLE. VI: LOAD AT CRACK AND LOAD AT BURST (FOR SAMPLES OF EXPERIMENTS 1 THROUGH 8) †

Sample	Load at Crack kg	Load at Burst Kg
Control	4.0	8.9
1	2.15	8.15
2	4.15	11.75
3	4.6	8.9
4	4.1	7.6
5	4.1	10.25
6	4.6	9.95
7	3.45	10.1
8	5.9	14

† Leather Industry Incubator, College of Engineering Industries and Technologies at Sudan University of Science and Technology.

TABLE. VII: CHEMICAL ANALYSIS OF SKINS (FOR SAMPLES OF EXPERIMENTS 1 THROUGH 8) ††

Sample	Moisture Content%	Ash Content%	Fats Content%
Control	3.5	10	6
1	6.2	33.7	2.0
2	7.5	23.8	1.8
3	6.5	21.0	1.7
4	7.9	19.7	2.0
5	6.0	20.1	1.8
6	5.1	22.7	1.9
7	5.1	24.2	1.6
8	12.2	26.7	1.9

†† Leather Industry Incubator, College of Engineering Industries and Technologies at Sudan University of Science and Technology.

TABLE. VIII: LOSS ON IGNITION (LOI) ‡

Sample	Loss on Ignition (LOI)%
Indian Fly Ash	1.16
SUDANESE FLY ASH 1	22.49
Sudanese Fly Ash 2	28.2

‡ Institute of Engineering Research and Materials Technology (IERMT) at the National Centre for Research.

TABLE. IX: ANALYSIS OF BOD & COD ‡‡

Liquor	Sample	BOD mg/l	COD mg/l
Soaking	Control	3200	9250
	Treatment 7	2500	7800
Unhairing	Control	7800	11750
	Treatment 7	6200	8125
Reliming	Control	7000	10875
	Treatment 7	4100	4500

‡‡ Institute of Engineering Research and Materials Technology (IERMT) at the National Centre for Research

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IV. DISCUSSIONS OF RESULTS

From the analysis of the randomly collected samples of fly ash (from the fly ash collected from Garri Station), it was found that there were many useful materials present in It, e.g. Na_2O, K_2O, Si_2O, CaO, Fe_2O and SO_4-S (see Table. I). In addition, it was found that this fly ash is highly alkaline, pH=11.5 (Table. II). Therefore, this fly ash can be considered as a valuable by-product, which can be used for many purposes.

Looking at Table III, it was found that the degree of unhairing in Treatments, 1, 2 and 3 (where only fly ash was used) was good but slight mechanical action was needed. In treatments 4, 5 and 6 where sodium sulfide was introduced with different percentages viz 0.5%, 1% and 2% plus the fly ash, it was found that the degree of unhairing was very good plus very slight mechanical action.

In treatments 7and 8, where normal sulfide percentage plus 5% fly ash were used it was found that the degree of unhairing was excellent and this indicates that the fly ash can be used safely in replace of lime in case of the hair pulping technique and in place of both the lime and kaolin in case of the hair saving process.

Regarding the tensile strength and elongation, it was found that all the tensile strength values were better than the control sample values. As for the elongation all the values for treatments were higher than the control value except Treatment 8, 59.5% is less, but it falls is within the standard acceptable limits (60%).

Regarding the load at crack and burst Table VI, the results obtained were found to be even better than the control, except Treatment 1, where the load at crack was found to be 2.15 kg and this may be due to the nature of the skin itself.

Considering the chemical analysis Table VII, it was found that, the moisture and the ash values, while the fat values are less than the control, were higher than the control and this may be due to the high filling effect of the fly ash (very small particle size) and the high degree of absorbency of the fly ash.

From Table VII, it clearly shows that there was a huge amount of an unburnt carbon presence in the Sudanese fly ash compared to the Indian fly ash.

Considering the BOD and COD analysis, from Table IX the values of Treatment 7 obtained for soaking, unhairing and reliming processes were found to be less than the control values and this showed that there is a considerable reduction in pollution load.

V. CONCLUSIONS AND RECOMMENDATIONS

In this paper, the fly ash from Garri Station is found to be highly alkaline (pH = 11.5), hence it was the idea behind using it in tanning to raise the liquor pH. It was applied in three stages of the tanning process. The fly ash was used instead of sodium sulfide in the main soaking and as a replacement of lime in both the unhairing and reliming.

The produced leather was tested and most of the results were found to be good compared with the control sample, and most of the results were within the standard limits. Besides reducing the cost of the lime and sulfide, there was a considerable reduction in the BOD and COD levels the liquor of the three stages that fly ash had been used compared with the liquor of the control sample, which reduces environmental pollution.

Further experiments need to be carried out for reuse of liming liquors several times after being discharged by reducing the quantity of chemicals and adjusting the pH by adding fly ash. Study the reasons of the large amounts of unburnt carbon (LOI) present in the fly ash from Garri Station and develop a technology that can separate carbon from the fly ash. Fly ash with low value of LOI could be used as a construction material which saves a lot of money besides solving environmental problems caused by dumping it in open yards.

The fly ash from Garri Station is alkaline in nature so it can be used in agriculture to adjust the pH of the acidic soil, and also it can increase soil water holding capacity. Fly ash could be used as a landfill; roadways are the biggest applications area and that would save a lot of money annually. Fly ash is composed of oxides compounds,

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so further studies could be carried out for using it as coloring material. Comparison of cost effectiveness between using fly ash and lime (Ca (OH)2).

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ABBREVIATIONS

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
FA	Fly ash
TSS	Total Suspended Solids

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