**Characterize and utilization of chrome shaved leather waste for block production –at ETHIO-LEATHER INDUSTRY PLC (ELICO-Awash Tannery)**

BY

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# Abstract

Chrome shaving waste is one of the highly generated solid wastes from the Leather industry. There is no proper utilization of these huge amounts of waste. It has been found that leather chrome shaved tannery waste is one of the good replacing materials in the construction industry. The objective of this study was an attempt to investigate the characterization and utilization of chrome shaved lather waste for solid block production, by using a raw material of chrome shaved leather waste, cements, aggregates and water as binders. In this investigation the sequence for the production of block clearly explained Chrome characterization such as ash content, moisture contents, PH. Chrome content, FTIR, SEM, DSC/TGA were done then mixing of raw material. Raw materials requirements are Ordinary Portland Cements, fine aggregates, coarse aggregates, Chrome Shaved and Water with a water cement ratio of 0.45. The constructed concrete block was also determined experimentally using standard methods as per standard ratio of 1:1.33:2.07 water to cements ratio 0.45 were used. The various percentages of chrome shaved leather that use to cast the specimen are 0%, 5%, 10, %, 15% and 20% three each quantity of Size of block 150 mm x150 mmx150 mm, 150 mm diameter by 300 mm and cured for 7th and 28th days and Finally Physical testing of block; compressive strength, tensile strength, density, moisture content and FTIR, DSC/TGA were conducted, summarized and analyzed by using tables, excel graphics. Results show that for 28th days maximum compressive strength achieved 37.33 N/mm2 by 15%, split tensile strength of block that’s achieved maximum for 28th days 4.20 N/mm2, density of the block at 15% achieved 1905.6 kg/m3 and water absorption 9.2 %. In the present study utilization of chrome shaved waste suitable for health and safety working conditions for worker and reducing environmental pollution as well as, chrome shaved fibers that are used as a reinforcing agent with block concrete so that there is a significant increase in the structural properties of block concrete. In other hand leather chrome shaved tannery waste is abundant in nature; a proper replacement of tannery waste over the fine aggregate not only reduces the tannery waste but also reduce demand for fine aggregate. The concrete produced due to this replacement have reduced weight and also possess higher strength than the conventional solid concrete block.

**Keywords**: Leather industry, Leather solid waste, Environment, Characterization Block, Toxicity of Chromium.

**Introduction**

The tanning industry generally uses hides and skins as raw materials for the production of stable commercial product called leather, which are the by-products of meat and meat products processing industry. In this respect, the leather industry could have easily been distinguished as an environmentally friendly industry, since it processes waste products from meat production (Vanitha1, 2012).

Tanning industry has been categorized as one of highly polluting because different chemicals has been used during tanning process and different solid, gaseous and high number of liquid wastes are generated which have an adverse effect on the environment (Ozgunay et al, 2007). The different chemicals that have been used in leather processing are salt for preservation of skin/hide which are cause for pollution load of total dissolved solid and chloride in water, other major polluting chemicals are lime, sodium sulphide, sulphuric acid, Ammonium sulphide, ammonium chloride, Chromium sulphate, non-ionic wetting agents, bactericides, synthan, resin, polyurethane, formic acid, binder, pigment, wax and enzyme (Huq et al, 1998).

High amount of solid waste is generated during tanning process in which out of the raw material only 20-25% is converted into finished leather 75- 80% is dumped to the environment. These tannery solid wastes have different characteristics because different chemicals and mechanical processes that are applied to the raw hides/skins. Solid wastes generate in tanneries mainly include raw trimming, fleshing, chrome shaving, buffing dust, crust trimming and finished trimming. The solid waste generated during leather processing containing these hazardous chemicals if they are not currently in Ethiopia there is no significant work done in utilizing this huge number of wastes. So that every tannery is disposing their solid waste directly to the land together with other municipal solid waste and some tanneries are using nearby river for dumping their solid wastes because there is no designated site for the disposal of hazardous waste (Tadese, 2003). And some of the tanneries are burning it in surrounding area in order to minimize the volume of wastes and transportation cost this in turn causes the oxidation of Cr (III) to Cr (VI) which cause carcinogenic effect to human body through food chain (Anita Singh et al., 2010).

Improper disposal of these leather wastes causes environmental pollution; therefore, proper optimized utilization of these wastes into value added end products will be a promising solution (Knagaraj et al, 2006).The objective of this study was to prepare solid concerts block using chrome shaving waste. The study aims to convert toxic chrome containing chrome shaving waste into a useful product, thereby reducing environmental pollution. Leather solid concerts block was prepared from chrome shaving waste, in combination with cements, water and aggregates enhance its mechanical properties. The products were characterized for their physic-chemical properties using FTIR, DSC/TGA and SEM. Mechanical properties such as compressive strength, tensile strength, water adsorption and density properties were also assessed.

**Literature review**

**Overview of the Tannery Process**

Tannery process is a process of converting animal skin and hides into non putrescible a stable commercial product called leather. The technologies used by all tanneries are not the same but there are some common operations in leather making activities. Before leather processing the cured skins and hide arriving the tannery are trimmed to remove unwanted materials and long shanks. Leather making processes are classified in to four main categories. The four main leather processing categories are Beam house operation, Tanning, post tanning and finishing (Covington, 2009).

**Leather Chrome Shaving**

Definition of Leather Chrome Shaving Waste After chrome tanning the chrome tanned leather will be shaved. Shaving evens the skins thickness and for hides also permits greater precision than is possible by splitting. This savings and splits will contribute highly to the total solid waste generation of the tannery. Chrome shavings are small, thin pieces of chrome tanned fibrous matrix of collagen formed during the levelling operation. Chrome shavings primarily consist of chromium and protein, which could be treated to give the potential resources of collagen protein and chromium. Unlike hide processing, sheep skins are shaved after re-tanning processes are completed (i.e. it is shaved at crust stage). The thickness at which shaving machine is set depends on the type of the end use of the finished leather to be produced. Usually glove leather and garment leather are shaved to a thickness ranging from 0.40 to 0.55 mm and 0.60 mm to 0.80 mm respectively depending on the customer requirement. In order to determine shaving waste (dry shaving waste) generated per kilogram of wet salted sheep skin processed, a sample often pieces of crust leather were randomly taken from different batches of crust leather prepared for shaving process and weighed before and after shaving operation.

**Characterization of Leather Chrome Shaving Waste**

 These wastes can be utilized with or without the presence of chromium. Attempts have also been made to reduce potassium dichromate using chrome shavings directly to give a chrome tanning agent product, usable in the tanning or retaining processing of leather industry. Prior research has demonstrated that it’s an effective way to acid hydrolyze chrome shavings into a chromium-containing protein hydro lysate which can also be reused in retaining processing. It’s found that it’s cleaner and more economical to separate the protein-bound chromium by the treatment of alkali or enzyme and use the protein and chrome cake or chrome sludge for several applications (Deqiang Su, Preparation of protein Retaining agent by Grafting modification of collagen hydro lysate extracted from chrome shavings) Land application and disposal of solid, chromium-containing tannery wastes has been widely practiced during most of the twentieth century. This is a rather expensive and environmentally inappropriate way of handling a waste material that has the potential for reutilization. In addition, the costs of disposal will continue to increase as fewer landfill sites can be found and the cost of transportation increases. About 75 % of the chromium containing solid waste is produced when the tanned hide is shaved to a uniform thickness. These chrome shavings are small particles, in a variety of shapes, mainly consisting of collagen cross-linked with Cr (III) complexes. (Cabeza, 1998). Chrome shavings hydrolyzed using magnesium oxide.

**Utilization of Leather Chrome Shaving Dust**

Tannery wastes normally contains only trivalent chromium. The production of chromium containing solid wastes (including chrome shavings) in a tannery has been recognized as a problem for many years but recently pressure from environmental authorities has given the problem increasing urgency. As a result, many scientific groups have oriented their research to find a suitable for processing to recover their constituents but the economics of the process is very important for industrial implementation (Cao et al. 2005). The chrome shaving waste is one of the major solid wastes generated during the leather processing. The chrome shaving waste mainly consists of collagen and chromium in the trivalent state, it forms complex with the collagen which is responsible for the formation of leather. This complex could be treated to give the potential resources of collagen protein and chromium (Kanagaraj, Velappan et al. 2006).If these proteins and other chemicals are not treated properly it will pose hazardous problem to the environment.

There are significant approaches in preventing environments pollution from the pollution prevention hierarchy the idea of prevention is better than reuse, reuse is better than recycling, and recycling is better than disposing of the wastes (Rao, Jha et al. 2007). Proper waste management and waste treatment methods are of utmost import .Varies technologies have been used to utilize 23 chromium containing leather wastes that helps to solve difficulties related to chromium containing solid wastes. The presence of chromium in wastes creates difficulty in disposing to landfill and incineration (Chaudhary et al. 2013). The chrome shaving can be managed in two ways. The one is by disposing to landfill with compliance to good management practices and the second is up gradation by viewing the waste as potential raw material serving either existing or new market.

**Toxicity of Chromium Containing Tannery Waste**

The utilization of chromium in tanning procedures accelerates the mobility and transport rates of chromium, which by far exceed the rates of natural cycle

|  |  |  |  |
| --- | --- | --- | --- |
|   |   | Sources | Total amount (Kg) |
| S.N | Types of CCTSW | Hide production | Skin production | Waste water treatments (Kg) |   |
| 1 | Wet shaving | 799,344 | 192,067 | - | 991,411 |
| 2 | Wet trimming | 327,600 | 44,712 | - | 372,312 |
| 3 | Crust shaving | - | 82,555 | - | 82,555 |
| 4 | Crust trimming | 76,752 | 33,696 | - | 110,448 |
| 5 | Finished leather trimming | 28,829 | 7,582 | - | 36,411 |
| 6 | Buffing dust | 12,575 | - | - | 12,575 |
| 7 | Waste water treatment sludge | - | - | 481,440 | 481,440 |
| Total |   | 1245100 | 360,612 | 481440 | 2,087,152 |

Source: (Wang et. Al., 2007)

**Chromium Containing Tannery Solid Wastes Management Practice**

There are a number of concepts about waste management, In order to guarantee a successful and proper integrated solid waste management plan; some of the most widely used concept in waste management includes the waste hierarchy. The waste management system refers to the ‘3 Rs’ reduce, reuse and recycle. It classifies waste management strategies according to their desirability in terms of waste minimization. Thus the waste management is based on this concept of hierarchy of options. Not producing the waste in the first place is the most desirable alternative. If once it is produced waste is increasingly being considered as a valuable resource to the industry and a major economic sector. Therefore, dealing with the waste not only has environmental positive effects but also economical, creating jobs and business opportunities (Onyuka 2010).Current solid waste management practice in Ethiopia is very weak. They have disposed there solid waste in an open dumping site together with municipal solid waste and some have burn it together with other dry solid waste.

**Methodology**

The raw materials and equipment used for the preparation of LCTSW of concrete solid block were leather Chrome Shaved, cement, fine aggregates, course aggregates and water as raw material. Chrome shavings were collected from awash Elico Awash tannery, aggregates was collected from Bahir Dar market places. Machineries used: Mixer, convection oven (dryer),Leather grinding machine, plate, tamper road, sieved machine, compressive strength, split tensile strength, water absorption and weight balance of aggregates were used to prepare the block. Chemicals: magnetic stirrer, Grease, sodium hydroxide (NaOH 99.97%)), urea, sulfuric acid (H2S04 98% m/m), calcium hydroxide (CaOH2), water (H2O), nitric acid (HNO3, 70% m/m), per chloric acid (HClO4 70% m/m), Ortho phosphoric acid (90% m/m) were purchased from the market. All the chemicals and reagents that have been used for laboratory experimental analysis were analytical grade. Different instruments were used for the physic- chemical analysis of the raw material. Such as scanning electron microscopic (SEM- JSM-IT300), Thermo Gravimetric Analysis (TGA), DSC (Differential Scanning Calorimetry), Fourier Transform Infrared (FTIR, Shimadzu, Japan IRAffinity-1), Digital pH meter, kjeldhal distiller and weighing balance.

**Results and discussion**

The result of block As indicated on the Figure water absorption, density of Block concrete at control sample (LG 0%) at 28th days achieved 7.27 % and 2417.778Kg/m3 respectively, when percentage of chrome shaved increase water absorption of block slowly increased until LG15%,

For density of the concrete block also decreased when chrome shaved waste slowly increased in percentage until LG15%, so decreased by 14.96% of the normal concrete mix (LG0%). when percentage of chrome shaved increase water absorption of block increased by leather chrome shaved waste at LG15 is 9.2% and increased by 26.54% of the normal concrete mix, this indicate that result range between the standard ISO 2185 (Bureau of Indian standard, 2005).So the block has better performance at LG15% for both block density and water absorption characteristics test.



 Figure 1: 28th Water to density curve

 Figure 2: 28th Compressive to split strength curve

Compressive and split tensile strength at control sample block 30.04 and 4.2 N/mm2 respectively both characteristic of block value increased slowly until they reached LG15% which is maximum value achieved then, decreased quickly this indicated that when the value percentage of leather chrome shaved waste increased compressive and split tensile strength increased unit it reached peak value of LG15%, Maximum compressive strength achieved by leather chrome shaved waste at 15% is 37.33 N/mm2 and increased by 24.267 % of the normal concrete mix (LG15%), maximum Split tensile strength achieved by leather chrome shaved waste at 15 % is 4.2 N/ mm2 and increased by 88.3 % of the normal concrete mix (LG 0%) So this block has better performances characteristics at value of LG15%.



Figure 3: FTIR value of LG15% LCSWB



 **Figure 4: DSC value of LG15% LCSWB**

**Conclusion**

The disposal of tannery solid waste can be done safely without causing any pollution to the environment. Tannery solid waste can be used effectively in the concrete block construction field. Physical(FTIR,DSC,TGA) and Mechanical characteristics of chrome shaved waste block were done as result show that compressive strength is increasing as increasing leather chrome shaved waste until maximum compressive strength achieved at 28th days LG 15%. Split tensile strength of leather chrome shaved waste block at 28th days increased by 88% of control block as well as increase in Tannery waste in a solid concrete block from 0% to 20% decreases the

There is no significant works done on utilization of solid waste density of the concrete from 2417.778 Kg/M3 to 1738.66 Kg/M3. Water absorption of leather concrete block increased by 26.54% of control block, this show that the presence of collagen fiber in leather waste increased water absorbability, but the result is found under range of Standard value.

In general, the results of this study have revealed that the tanning industry generates solid chrome shaved waste is the major tannery waste, instead of dumbing or burning to environments its better use for construction material, this lead minimized of solid waste presences in the tannery industry, protection of the environmental and in other way it has been good replacements material for construction industry, Tannery waste solid concrete block can reduce the use of fine aggregates or sand in concrete block and results in lightweight concrete block.

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