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Options for Utilization of Tannery Sludge

M. Jothilingam, Pratheeba Paul, G.Janardhanan

***Abstract:** At global level, the India has amassed the largest livestock and their skins and hide are used for the manufacture of large scale leather and 75% of tanneries in India are the small scale tanneries. The leather industry in India with annual turnover of more than 12 Billion dollar has a cumulative annual growth of about 3.09% in the last five years and 2nd highest manufacture of footwear and garments in the entire world, which leads to foreign exchange. Tannery sludge generation about 150000 TPA causes chromium pollution and contaminates water bodies & soil and risk to eco-system. Further, that affects the agricultural productivity and therefore, Tannery has been classified under the red category. The Supreme Court finding of fact resulting in the closure of polluting tanneries has led to unemployment problem and affecting national GDP. The present tannery sludge disposal methods like Composting, landfill, anaerobic digestion systems are not providing the satisfactory result. Reuse of industrial waste is advocated worldwide and in some of the countries as a remedial measure solidification and stabilization concept is adopted for reducing heavy metals from industrial waste. In this review the outcome of various research on the properties natural clay, ceramic and cement based stabilization of the tannery sludge has been discussed and the research gap is also identified .*

I. INTRODUCTION

The industrial waste generation is ever increasing due to setting up of new industries to meet out the national demand and based on the government export & trade policy to create employment opportunity and revenue generation. The risk of industries pollution to the persons and also the atmosphere are often reduced by increasing the effective utilization of industries waste for the downstream method or alternative producing method As a part of waste to wealth concept the natural resources utilized for manufacturing of building construction material can be recycled by industrial waste materials after ascertaining their physical and chemical characteristics [1]. Leather industry is a foreign exchange earner and classified as RED category by the government authorities since it is the most polluting one [2]. India is that the second massive manufacturer of animal skin and merchandise since it's holding the biggest livestock of 21% from larger animals (Buffalo & Cow) and 11% from little animals (Goat & Sheep).

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* Correspondence Author

M. Jothilingam*, Assistant Professor (S.G), Dept. of Civil Engineering, SRM Institute of Science and Technology, Chennai-600089, India

Pratheeba Paul, Professor, Dept. of Civil Engineering, Hindustan Institute of Technology and Science, Chennai-603103, India

G.Janardhanan, Associate Professor, National Institute of Technical Teachers Training and Research, Chennai-600113, India

Leathers are created from skins of animals like cow, buffalo is known as hides and goat and sheep referred to as skins by tanning method [3]. As per survey, 75 % of tanneries are portable units and 20 % are mediums scale remaining 5 % are large-scale units. Out of these productions over all 65 % of leather production in the country is from small and micro sectors and 88% of the tanneries are in the states of, West Bengal, Tamil Nadu and Uttar Pradesh [3]. The chromium pollution from the waste water of tanneries affect aquatic environment of the surface water bodies, ground water and affect the soil properties and agricultural crop yield if not adequately treated to the prescribed standard [2].The tannery effluent treatment plants generate large quantity of sludge and the solids content will depend upon the raw material, type of process adopted, chemicals used in the process and other in-plant control measures. In India, 600 million kg of raw skin and hide every year generating around 50 (MLD) Million Litres per Day of water waste and 305 million kg of solid waste. The waste material effluent from tanneries is that the vary of 30 – 120 kg of BOD and 75 – 320 kg of COD per ton of raw hide or skin processed. Tanner has develop the environmental issues has become tougher once the directions of apex court resulting in the closure of polluting tanneries throughout in 1995 [2]. According to a study it was found that, tanneries have caused varying degrees of damage to 15,600 hectares of agricultural land owned by around 32,000 people. The water absorption capacity of tannery sludge is very less and taken more than 65 years to get degrade and 100 years for complete degradation and so it is not advisable to be dumped in land fill its lead to affect the natural groundwater table. During at high temperature the tannery wastes are releases certain gases like SO, CO, etc. it causes huge problems to living things like carcinogenic effect, irritation to eyes etc.[4]. A number of efforts for utilization and safe disposal of sludge are planned, practiced, tested and applied at pilot and industrial scale, land application, composting, anaerobic digestion, brick creating, etc., none of them providing satisfactory results. There is no standard and effective solution has been found for the utilization of sludge waste. Tannery sludge waste characteristics are varying from region and country level as per ETP and regulations [5]. Presently reuse of the dangerous industrial waste is advocated worldwide. Solidifying in natural process, the wastes are mixed with enormous cementitious materials to get a replacement, with increase the physical properties of wastes, during which the concentration of the significant metal is reduced. Based on this concept research study has been carried out by mixing the industrial sludge with cement concrete and utilized as concrete block as an effective solution in reducing leaching of heavy metals. This approach may also serve as economically viable and environmentally friendly option. However, detailed study seems necessary for determining the proper mix design and methodology concerning the stabilization of the sludge with concrete without significantly sacrificing the strength [4].

From the literatures it is observed that technologies have been developed to convert waste materials to binding material, ceramics, glass-ceramics will acquired in the place of economic importance. The hazardous industrial wastes are destroyed and heavy metals are immobilized and stabilized by ceramic and glass technologies with potential for market exploitation [6]. The sludge from water treatment plant is similar in chemical composition present in clay and this will be used in the manufacturing of clay bricks [7].Likewise bricks are made by cement ,quarry dust and tannery sludge and it is used in the construction as common mud brick. The sludge is the way for disposal of tannery waste in safer zone and it cannot develop any environmental pollution by making sludge bricks at affordable cost for the replacement of concrete masonry block [8] and possible to reduce the river sand in the production of concrete while using tannery sludge as partial replacement to river sand.

II. PHYSICAL AND CHEMICAL CHARACTERISTICS OF TANNERY SLUDGE

2.1 Composition

The sludge composition measures are modified from one country to a different counting on the processes adopted and chemicals applied.[9] Therefore, chromium has an important constituent in the sludge as found in the alternative studies [1]. The particles size of the sludge is larger than that of the clay soil being used for brick manufacturing and the components are similar with different quantities as shown in Table 1. Tannery sludge is used as partially replaced material in brick manufacturing. The presence of organic constituents in the mix is likely to reduce the strength of the concrete [4].

Table 1 Presence of chemicals in soil and tannery sludge

Composition	Tannery sludge (%)	Soil (%)
MnO	0.23	0.12
CaO	26.1	2.2
Al_2O_3	0.49	13.28
SiO_2	3.52	63.7
SO_3	28.7	0.57
Cr_2O_3	3.4	0.05
TiO_2	0.4	1.3
MgO	1.7	4
ZnO	0.09	0.03

2.2 Test methods

The water molecules and the organic matter of clay and sludge waste were resolved by APHA system [10]. From the earlier study, the optimum moisture content is determined as per the AASHTO T265 [11]. X-ray fluorescence is used to find the chemical contents waste materials. For metal analysis, 5 gms of dry sample were mixed with acid HNO3 and HCl in the ratio of 1:3 for 24 h, and distillation water is added at 400 ml and its heated upto 2 h to prepare a sample of 500 ml solution. This solution was then filtering with 0.45 mm filtration paper then the sample were taken to describe the presence of metals like (Cr ,Zn, Pb, Ni, Cu, As) done as per Atomic Absorption Spectrophotometer (AAS) [12]. From the literature study, to find the plastic condition of the sludge clay mix is done by Atterberg limit tests are carried out as per ASTM D 4318 [13].

III. LEACHABILITY STUDIES

The pH value, alkalinity, organic percent, sulfate, sulfide, nitrate, chloride and silica are reported to have bearing on the strength of concrete as well as on the leaching potential of sludge [4]. The develop concrete with the addition of different percentage of sludge shows high pH value from 12.5 -13.5. Therefore, the stabilization of metals occurred in a high alkaline system [4]. Atomic Absorption Spectrophotometer can be used to determine the total heavy metal concentration [4]. The presence of total chromium concentration can be found by Inductively Coupled Plasma Mass Spectrometry [14]. From the earlier study, the leachability and toxicity tests were done by two method that is toxicity characteristic leaching procedure as per Netherlands tank leaching test NEN 7345 [15]. From the cement mortar the values of chromium leaching meet the necessity for non-dangerous material prescribed in 33/EC/2003 then its documented in various countries Chromium, Lead and Cadmium have considerable potential for leaching. Concrete mixed with 20% of sludge/cement showed the highest concentration of chromium and Lead [4]. The Lead was found to be leachable with ceramic samples includes of 30% tannery sludge and it is recommended [6]. The leaching of metal could concern as metal containing sludge waste was induced to the complete product. The experiments suggested that, the metal presents it will effectively stable by incorporating the sludge mix in the production of clay brick.

IV. MIX CHARACTERISTICS

Tannery wastes are collected and it is used as fine aggregate in this research. After sieving with the size of 2.36 mm passing materials are collected to replace the river sand [8]. The density of tannery sludge is less when compared to river sand. The sludge content of the sludge mixed concrete was varied from 1% to 20% by weight of cement. Water/cement ratio less than 0.50 produced too harsh concrete with inconsistent mixing of the materials. Inadequate water/cement ratio leads to improper bonding between sand and sludge. The slump increased gradually for addition of more than 10 % of sludge [4].

More than 10% of sludge addition indicates an unacceptable value of setting time. And the 5% of sludge addition gives good workability concrete. While addition of more tannery waste in the range of 0% to 20% for the production of concrete ,the density reduces from 2419 kg/m^3 to 1738 kg/m^3 [8]. The presence of wet content affects the properties of bricks. Further water molecules exchange the air from the soil voids. When the maximum degree of saturation compound is attaining, the water engaged the place which might well be occupied by the soil particles. Consequently, associate degree possible quantity of blending water molecule within the brick manufacturing process is typically more demand This lead to magnified the density, the water absorption and harden strength of the concrete. The plasticity index decrease when the sludge waste are maximum in the mix this will be done Atterberg test. As per ASTM C403 the average time of initial setting varies between 169 and 252 minutes, and the average time of final setting varies between 240 and 341 minutes in the lab condition, temperature 20 - 25°C. The initial setting time and final setting time is gradually increased because of adding sludge in the concrete [4]. If the setting time of the concrete faster the development of strength gets delay [8]. The manufacturing of bricks with sludge is used to find out the effects of mechanical and physical properties of sludge waste present in the concrete and also the sludge quantity allow the bricks for advantageous mechanical properties of building material [16].

V. MECHANICAL PROPERTIES

5.1 Compressive strength

The harden properties of concrete has an important one to check the qualities of building material. It can achieved inversely proportional to sludge and directly proportional to firing temperature. It will be done to reduce the porosity and increase the bulk density resulting at maximum temperature [17].The strength of the bricks were 8.7 N/mm^2 and 10.29 N/mm^2 as per the ASTM 62-2012. The bulk density of the bricks increases when the heating temperature is high. It was observed that the 3rd days and 7th days compressive strengths gradually decreased with the addition of sludge in concrete. But in, 28th the days the compressive strength almost same as the sludge free concrete for 1% of sludge addition and then decreased gradually with the increased amount of sludge content [4]. This result proves that, the addition of sludge up to 5% is produced workable structural concrete with high compressive strength. Up to a 6% addition of tannery sludge increased the compressive strength up to 26% with more density and UPV as 4% [18]. The tannery waste was utilized as partial replacement to river sand is eventually increased and the optimum replacement is upto 10% [19]. From the literature study, the mortar compressive strength in the presence of tannery sludge is higher when it was compare to the normal mortar. From the studies on ceramic bodies, it is found that the shrinkage effects increases with the samples firing temperature [8]. The ceramic materials include the sludge content 30%, with the less densification, shown maximum linear shrinkage in this temperature. Bending strength of ceramic samples get high with the heating temperature reaches more, because the presence of porosity nature of the material. The ceramic and tannery sludge bricks have the similar mechanical properties. These results obtained from the Nondestructive test (UPV and Rebound Hammer) It proves that the quality of the concrete will not affect in the presence of tannery waste. The Mechanical properties on concrete gradually increased because of the presence of waste upto 15% and if addition of these wastes the strength parameter gets decreased. [8]. According to a study conducted on geopolymer specimens, after calcination of geopolymer contains 20% of sludge specimens at 200oC, the strength of the harden concrete is higher at 58.55 MPa. Geopolymer with sludge are same as in metakaolin form geopolymer. Similar reports the solid product give maximum compressive strength and impermeability [14].

VI. DURABILITY PROPERTIES

6.1 Water absorption

In this research the water absorption conducted for the purpose of thermal treatment on ceramic materials [6] have to find out that the absorption reduce notably, when the heating process is reached at higher than 1100oC. Sludge addition is more the water absorption also gets increased. The maximum possible replacement of tannery sludge mortar is 6 % [18].The amount of water penetration within the brick is a smaller amount, additional are its resistance to weathering agenesis and even more for durability of the bricks [20] The water absorption of the bricks are maximum in sludge addition there by increasing its susceptibility to weathering agenesis. In same time, the absorption was find to be reduces when firing temperature was maximum. Because the development of amorphous phase at maximum heating temperature [21]. Normally, sludge contains a high quantity of organic matter that causes pore in the bricks, at maximum temperatures and these spaces favor to absorption of water as shown in Figure 1. Same trends also reported, in water absorption with sludge waste in bricks and various construction materials has found in other studies also [6, 22, 23, 24].

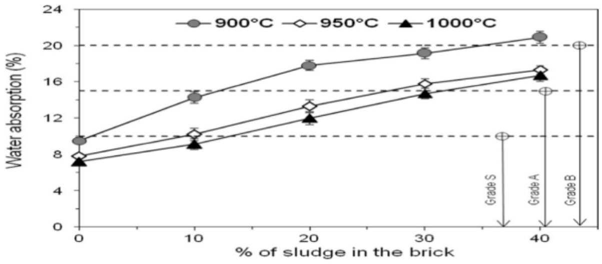

Figure 1. Various temperature of Sludge bricks water absorption

The chromium leached on sludge waste based geopolymer are increased with maximum of NaOH [14]. In the alkali solution presence of pH has small impact on the strength of sludge with geopolymer concrete, the harden strength reduces gradually as the soaking time increased.

6.2 Efflorescence

The efflorescence development can diminish the performance and the aesthetic quality of engineering material. Sludge contains inorganic salts which are able to get diluted in water and settled on the surface of building materials. Previous research state that sludge waste bricks heated at 1000°C are not susceptible for the formation of efflorescence and open to a wide range of atmospheric conditions..

6.3 Weight loss on bricks

The weight reduced in the bricks was found out when the percentage of sludge waste added at maximum. The mass reduces of the bricks was depends on the heating of material. [16]. the weight reduces because of the decomposition of organic and inorganic matter of tannery sludge and clay during the heating process [15, 30].

VII. MICROSTRUCTURAL CHARACTERISTICS

7.1 X-Ray Diffraction (XRD)

XRD has a successful process to find the crystalline structure of material. It helps to discover the crystalline material having crystal nature is more than 3 nm. It helps to find the crystalline nature and composition of chemicals [20]. XRD analyses shows that the mortar materials contained minerals are portlandite, quartz, ettringite, , dolomite, and the specimens are changed with tannery sludge waste as higher amount of portlandite, CSH and minimum count of ettringite, and less count of non-hydrated cement contents [12]. With the hydration reaction in the concrete, CSH and Ca(OH)2 are formed. CSH is the main constituent that imparts strength to the concrete as shown in Figure 2. Higher strength develops in concrete with the increased amount of CSH formation in concrete [25].

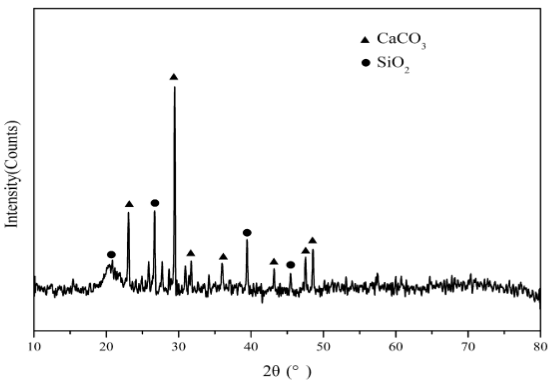

Figure 2. XRD pattern of tannery sludge

7.2 Mercury Intrusion Porosimetry

Mercury intrusion porosimetry as a destructive and non portable technique. It helps to find the total analyze of porosity in the concrete, volume of pores, pore size distribution, and surface area. It helps to find the porosity and diameter of the sludge waste materials. The TS with geopolymers concrete have a maximum number of mesoporous developed by the gap on geopolymers materials. The geopolymers with smaller median pore diameter and minimum average pore diameter were characterized by higher strength [14].

7.3 Thermogravimetric differential thermal analysis

The thermogravimetric analysis (TGA) can be used to analysis the changes in weight of the sample while heating. TGA calculate the weight changes in the materials at time of heating under a constraint atmosphere [25, 26]. According to a previous study, it is observed that silica ratio and sodium oxide ratio in the reaction system had a significant effect on the properties of the sludge waste with geopolymer. According to the TGA curve, the dried tannery sludge showed more than 50% mass loss. The heating organic matter available in the tannery sludge is the primary attribute for this loss [14]. The water loss at 200°C facilitated the condensation reaction within the solidified product, resulting in a light changes in the strength of the concrete. After the water molecules gets evaporated, the quality of the geopolymer decreases slowly and the mass also reduces because of dehydroxylation of Al-OH and Si-OH at mixmum temperature [27]. The compressive strength is decreased when the temperature is above 800°C due to the conversion of quartz to the lower intensity of nepheline and sodalite [14]. Figure 3 shows the thermogravimetric analysis tannery sludge waste, Geopolymer and solidified product.

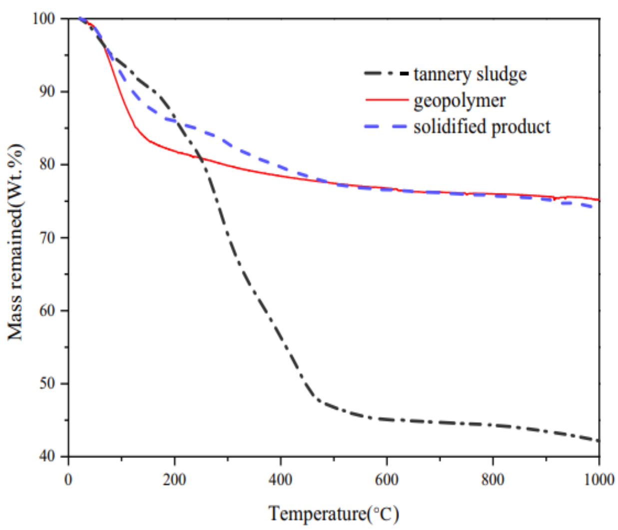

Figure 3. Thermogravimetric analysis for TS, Geopolymer and solidified product

VIII. ECONOMIC ANALYSIS

The brick manufacturing industries are the most maximum energy consuming field and generate high environmental related problems [28]. The tannery sludge wastes were introduced in the brick manufacturing process and reduce the energy consumption. When compare with normal bricks the energy savings are ranges from 15 – 47% and it can be achieved with replacing the tannery sludge of 10 – 40% for production of bricks [16].

IX. CONCLUSION

- The tannery sludge content in the concrete the water absorption also increase and the compressive strength of the TS specimens get decreased. The tannery sludge waste bricks are to fulfill the needs of BDS and ASTM. The optimum replacement for TS-amended bricks without disturbing its mechanical properties is 10%.
- As per USEPA regulatory limits and Dutch regulations the leached concentration of targeted metals are find to be insignificant
- The XRD results shows that, When compared with pure metakaolin-based geopolymer the sludge base geopolymer are in same layer structure. This will proves that the solid products gets higher compressive strength and impermeability
- TS with geopolymer is the best process to reduce the tannery sludge waste , stabilize chromium ions, and convert wastes into reuse material.
- The presence of geopolymer it helps to harden the tannery sludge and used in the building material.

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