Solid waste Management in Leather Sector

Sekaran G[1], Swarnalatha S[2], Srinivasulu T[3]
[1 2 3] Central Leather Research Institute, Adyar, Chennai, India
e-mail: ganesansekaran@hotmail.com

Abstract

Leather industry discharge solid wastes to a tune of 07 kg/kg of raw material used. The solid wastes are non tanned collagenous and tanned collagenous .Land fill method, anaerobic digestion, thermal incineration have inherent problems to execute. The high concentration of trivalent chromium along with organic/inorganic compounds in tanned solid waste such as buffing dust, shavings and sludge causes severe ground water contamination in the case of land co-disposal and chronic air pollution during thermal incineration. In the present investigation, these tannery wastes were subjected to incineration at 800C in a Starved Air thermal incinerator under different flow rate of oxygen to optimise the flux of oxygen require to prevent the conversion of Cr^{3+} to Cr^{6+} (Combustion). The energy audit of incineration of wastes under the external supply of oxygen was carried out under different conditions. The calcined wastes were effectively solidified/stabilized using Portland cement and fine aggregate. The solidified blocks were tested for unconfined compressive strength and heavy metal leaching. Unconfined compressive strength of the blocks was in the range of 120 180 kg/cm^2. Leachability study through TCLP on solidified block was carried out to determine the degree of leachate and metals. The percentage of metal fixation was 99.1 99.9 % and dissolved organic concentration in the TCLP leachate was 55-66 mg/l. Index terms - Chrome shaving, bottom ash, sludge, starved air incineration, solid waste, leather industry.

Key words: Anaerobic Digestion, Thermal Incineration, Calcination Unconfined Compressive Strenght, Leachability

I. INTRODUCTION

Leather industry generates a significant quantity of solid wastes (0.7 kg / kg of hides or skins processed). They are classified into tanned and non tanned collagenous waste. Besides , The dissolved chromium and other spent chemicals namely proteins, poly phenolic compounds, surfactants, dyes, etc. present in the waste-water are removed through chemical precipitation technique using lime and ferrous sulphate, before the wastewater is allowed to enter the biological treatment process. The precipitated chromium along with the other organic compounds is discharged as primary chemical sludge (Chang 2001). The basic component of solid waste is protein. Hence, they undergo microbial degradation, may be at retarded rate. Options such as land fill, vermin composting, anaerobic digestion and thermal incineration were considered for disposal of solid wastes.

A. Landfill Disposal

Diversion of land for waste disposal would be physically impossible since areas with the largest concentration of solid waste would also be the areas with serious scarcity of vacant land. The implication, therefore, is that if the current methods of solid waste disposal persist, the waste would have to be carried over long distance, which would require the creation of a great deal of transport facilities and infrastructure. This would involve enormous additional finances. Land filling scenario faces the highest cost, which is explained by the combination of the overall high pollution emissions and low energy recovery. And also the available landfill sites rapidly reach their total capacity and the authorization for new site becomes difficult (Kirk 2002). Indiscriminate land filling leads to deterioration of water quality in neighbourhood areas of land fill sites due to contamination by leachates from the landfill sites. Land fill gas, which is 50-60% methane, contributes significantly to global warming. Hence, land fill disposal method has been discouraged by environmental experts and technological interventions were made.

B. Vermin Composting

Studies on the vermicomposting of tannery solid waste with cow dung and leaf litters have been performed using *Eisenia foetida*, and petrochemical sludge using *Eudrilus euginea* (Rajesh Banu et al.,2005). *Eisenia foetida* is an epigeic earthworm species which requires high moisture content, adequate amount of suitable organic material and dark conditions for proper growth and development. The solid waste had no deleterious effect on earthworms. The growth rate was poor (detention time was 60 days). The vermicomposted tannery solid waste (tannery solid waste 75%, Cow dung 17.5% and litter leaves 7.5%) had germination index for FM1 using tomato seedlings *(Lycopersicon esculentum cv* -PKM1) was 100%. It was observed that the chromium was leached into bottom of the bed used.

C. Anaerobic Digestion of Animal Fleshing

Anaerobic digestion consists of break down of biodegradable material by microorganisms in the absence of oxygen. This method has been applied for the treatment of solid waste (animal fleshing) and co-digested with secondary biological sludge. This process has advantage that it reduces the emission of green house into the atmosphere. Anaerobic digestion can be regarded as a non conventional energy source because the process produces methane and carbon-di-oxide rich biogas suitable for energy production helping to replace fossil fuels. The methane can be burnt to produce both heat and electricity, usually with a reciprocating engine or micro turbine. The residuals left after anaerobic digestion is nutrient-rich and can be used as organic manure. The negative aspects of anaerobic digesters are the careful control of the temperature, pH and organic loading rate of the influent and technical expertise. The biogas contains hydrogen sulphide which causes dry corrosion in the burners and thus it is required to scrub the gas before considered as fuel gas, adding to the capital cost. high capital costs and lower process efficiencies have limited industrial level application of this process. Anaerobic digesters fed with animal fleshing generated methane gas 46 L/kg and electrical power of 6 w/kg of animal fleshing.

D. Thermal Incineration

Capital investment of the thermal incineration process is only about $1/6^{th}$ of the total cost for the land filling scenario (Assefa 2005) .Therefore, tannery wastes like sludge, shavings and buffing dust can be thermally treated to reduce the volume to be disposed off . The thermal treatment of wastes involves incineration, gasification and Pyrolysis as a mean of disposal, while also recovering energy from waste. So the thermal incineration is considered as the cheapest alternative and attractive method for its simultaneous energy production and volume reduction of solid waste. The thermal incineration of solid wastes from tanneries needs a special attention on the issues such as release of toxic chromium (VI), halogenated organic compounds, poly aromatic hydrocarbons etc. into the environment (European IPPC report 2001) . The major species formed from Cr (III) during thermal incineration of solid waste are $Cr_2(SO_4)_{3(s)}$, $CrOCl_{2(g)}$ and $Cr_2O_{3(s)}$ which later accounts a path for the formation of Cr (VI) (Chen 2003, Skrypski-Mantele 1995) . In the present investigation, the chrome shavings generated from a garment leather manufacturing industry is subjected to starved air combustion to utilize its maximum calorific value as well as to inhibit the oxidation of Cr^{3+} to Cr^{6+}. The process produces bottom-ash containing toxic heavy metals mainly Cr^{3+} and partially burnt carbon. The highly toxic properties of ash prohibit its direct land co-disposal. Therefore, an effective solidification and stabilization of bottom ash was resorted to change potentially hazardous solid wastes into less hazardous or non-hazardous solids before it is disposed off as landfill (Ioaninides 2003, Filibelix 2000). Solidification is another process that as been considered as an alternative solution to the wastes containing heavy metals. In the present study the bottom ash was solidified and stabilized using Portland cement, fine aggregate, coarse aggregate and blue metal dust. The focal theme of the present investigation was on (i) To arrest oxidation of trivalent chromium to hexavalent chromium with simultaneous energy utilization from organic fractions in thermal incineration, (ii) solidification and stabilization (s/s) of bottom ash of calcined chrome shavings and its leachability studies.

II. ATERIALS AND METHODS

A. Source of Solid Waste

Solid wastes were collected from M/s. Sri Chammundi Leathers a Garment leather manufacturing Industry, Chennai.

B. Characteristics of Tannery Solid Waste

The samples were preserved after collection and brought to the laboratory for characterization. The characteristics of the solid waste were determined in accordance with Standard methods for the analysis of Water and Wastewater (APHA, AWWA, WEF 1998). The characterization of the dried solid waste (sludge, shavings and buffing dust) such as pH, moisture content, ash content, chemical oxygen demand (COD), Total Organic Carbon (TOC), chromium(III) [(Cr^{3+})] and chromium(VI) [(Cr^{6+})] was determined. Thermo-gravimetric analysis (TGA) studies were carried out to determine the thermal stability of waste.

C. Calcination of Tannery Sludge

The schematic representation is an experimental set up of starved-air thermal incineration diagram as shown in Fig. 1. The incinerator, of size 65.5 × 65.5 × 45.0cm, was made of stainless steel and could hold the maximum capacity of 2 kg of sludge, 0.5 kg shavings and 0.5 buffing dust that was used for the starved-air incineration. The dried primary chemical sludge was pulverized in a ball mill to pass through a screen size of 600µ. The pulverized sludge, shavings and buffing dust were loaded in a stainless steel (316 grade) vertical reactor of Weight 13 kg, which was placed in an electrical furnace. The tannery solid wastes were incinerated under starved air condition at 800 °C with a provision to collect and to treat the off gases discharged from the furnace. Adequate care was taken to avoid the conversion of Cr^{3+} to Cr^{6+} by flushing the furnace with nitrogen: oxygen mixture at a ratio of 90:10 (V/V). Here a gradual increase in temperature at six segments for about 9 h.

Segment I	:	Ambient temperature◦ 100 ◦C (rate of heating ◦C h- 1 for 1 hour).
Segment II	:	100 ◦C◦ 300 ◦C (rate of heating ◦C h- 1 for 2hour).
Segment III	:	300 ◦C◦ 400 ◦C (rate of heating ◦C h- 1 for 2h).
Segment IV	:	400 ◦C◦ 600 ◦C (rate of heating ◦C h- 1 for 1hour).
Segment V	:	600 ◦C◦ 800 ◦C (rate of heating ◦C h- 1 for 1hour).
Segment VI	:	800 ◦C (soaking for 2 h).

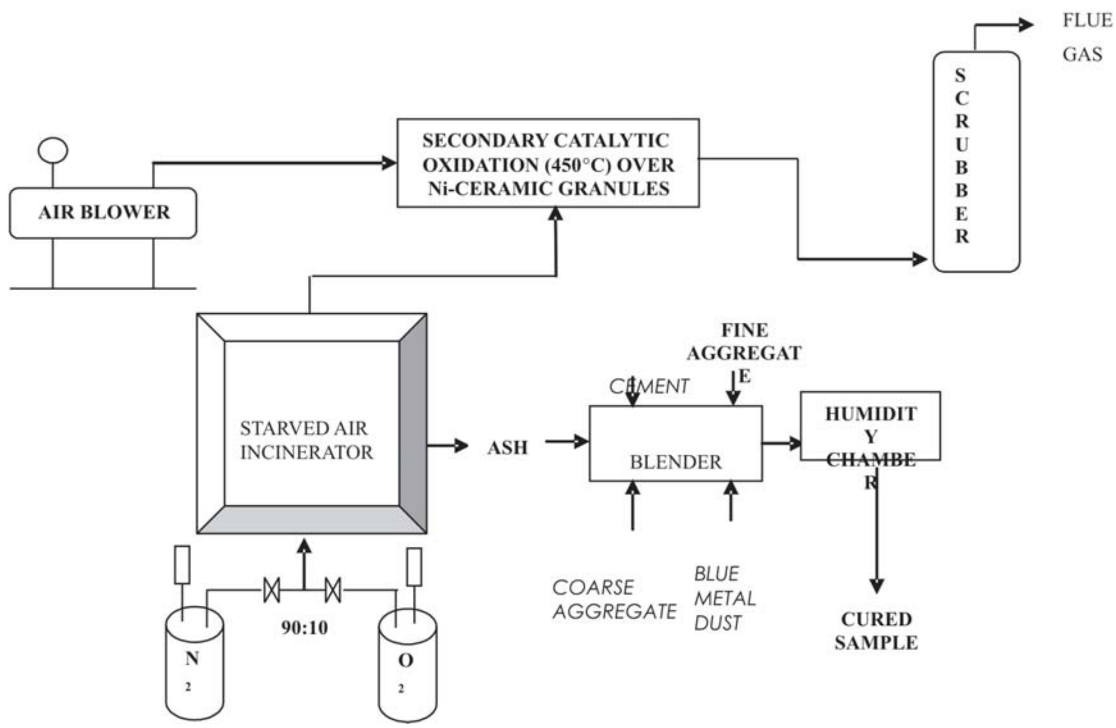

Fig. 1. Schematic Diagram of Starved Air Incineration Followed by S/S Process

The flushing of the gas mixture was stopped in the segment V& VI to avoid the conversion of Cr^{3+} to hexavalent chromium (Cr^{6+}). The energy consumption was recorded by means of an energy meter (India Meters Ltd., Chennai, India). The record of energy consumption and recovery, for different wastes (sludge, shavings and buffing dust) was carried out at airflow of 7.5 lpm and common weight of 400 g of solid samples was carried out in the present investigation. The bottom ash generated during the incineration process was collected in the bottom tray of the furnace. The flue gas from the incinerator was further scrubbed in a scrubber. The scrubber is made up of PVC of 1.5m height and 17.5 cm diameter to remove acidic vapors using alkaline water.

D. Solidification, Stabilization and Preparation of Concrete Blocks

The bottom ash of different solid waste (sludge, shavings and buffing dust) was collected from the furnace is powdered and content of ash was determined. calcinated bottom ash was mixed with binder in proportions. They were mixed in one third by weight of the volume of the brick mould. Casting was done by cold molding. Cold molding was used to prepare the solidified concrete blocks. Concrete blocks, measuring 7.5 cm×5 cm×10 cm was made using 3mm thick polymethacrylate sheet for cold molding. Binders used in this study such as cement 43 grade (RAMCO Cements, TamilNadu) and gypsum

were also used as binders for solidification of bottom ash because of their cheapness and availability. Different components used for brick mould namely calcined wastes .(sludge, shavings and buffing dust), course aggregate, fine aggregate, dust, uarry chip, and Portland cement/gypsum were used (in dry condition) .The components were mixed (in dry conditions) in a homogenizer until a

homogeneous mixture was produced. It was made into wet plastic mass using water and homogenized in an extruder and casted into molds. The casted blocks were removed from the molds after 2 days and cured for 28 days in a constant humidity chamber made of polyacrylic material. Unconfined compressive strength (UCS) of the cured concrete blocks was determined in accordance with the procedure of ASTM D2850. Strength of concrete specimen of different compositions were decided with help of UCS value.

E. Leachability Test for Solidified Waste

The leachability of the metals from the solidified samples of calcined ash brick was determined by a Toxicity Characterization of Leachate procedure test (TCLP). The TCLP method uses two different procedures, depending on whether volatile compounds are involved or not. In our case, the procedure when volatile compounds are not involved was used. The cured samples were crushed, powdered and homogenized to pass through a 600μ screen. The extraction fluid depends on the initial pH of the sample; in our case, all the samples had a pH 5.0 and, therefore, extraction fluid number 1 was used. This fluid was prepared by adding 5.7 ml of glacial HOAc to 500 ml of water without interference, then adding 64.3 ml of 1.0 M NaOH and diluting to a volume of 1lit. The sample and the extraction fluid (solid and liquid ratio of 1in 20) were put into a TCLP cylinder and placed in a TCLP rotatory agitator (10 rpm) for 18 h. After this period, the solid and the liquid phases were separated by filtration through a 0.60.8 μm borosilicate glass fiber filter. The liquid phase was analyzed for pH, COD and chromium up to 32 h.

III. RESULTS & DISCUSSION

A. Characteristics of Tannery Waste

The moisture content, ash content, COD, TOC, Cr^{3+} and Cr^{6+} of the sludge were 23.89 %, 23.3 %, 560 mg/g, 270 mg/g, 5.8 mg/g and BDL respectively. Gross calorific value of the sludge is 928 Kcal/kg. The elemental analyses of the sludge are Carbon 12.15 %, Hydrogen 1.392 %, Nitrogen 0.557 % & Sulphur 0.864 % & Oxygen 12.336 %.

The moisture content, ash content, COD, TOC, Cr^{3+} and Cr^{6+} of the shavings were 11.15%, 45.4 %, 840 mg/g, 315 mg/g, 10.68 mg/g and BDL respectively. Gross calorific value of the shavings 4096 Kcal/kg. The elemental analyses of the shaving are Carbon 37.23 %, Hydrogen 6.193 %, Nitrogen 6.443 % & Sulphur 1.422 % & Oxygen 25.0 %.

The moisture content, ash content, COD, TOC, Cr^{3+} and Cr^{6+} of the buffing dust were 37.38%, 43.4 %, 760 mg/g, 290 mg/g, 8.85 mg/g and BDL respectively. Gross calorific value of the buffing dust is 3838 Kcal/kg. The elemental analyses of the buffing dust are Carbon 42.8%, Hydrogen 8.099%, Nitrogen 8.113% & Sulphur 1.846 % & Oxygen 30.98 %.

B. Starved Air Combustion of Tannery Waste

Net heat energy change (q) is positive in the first stage, which means heat energy was absorbed by the system, it is due to the surface and bound water movement & also towards volatile inorganics present in the sludge. Net heat energy change (q) is negative in the second stage, heat energy released from the sludge components, which is associated with the combustion of the organic fraction of the sludge. Net heat energy change (q) is positive in the third stage; heat energy was absorbed by the system possibly for the decomposition of inorganic compounds, maintaining the reactor at 800 °C and for the heat retained in the ash as shown in Fig. 2. This says that the ultimate loss of heat in the starved air incineration is due to the combustion of inorganics, which takes place above 700°C as denoted below.

$CaCO_{3(s)}$ --------------> $CaO_{(s)} + CO_{2(g)}$

$\Delta H =$ +178.3 kJ/mol

$2FeSO_{4(s)}$ --------------> $Fe_2O_{3(s)} + SO_{2(g)} + SO_{3(g)}$

$\Delta H =$ 329.3 kJ/mol

$2Al(OH)_{3(s)}$ --------------> $Al_2O_{3(s)} + 3H_2O_{(l)}$

$\Delta H =$ +10.02 kJ/mol

$2Cr(OH)_{3(s)}$ --------------> $Cr_2O_{3(s)} + 3H_2O_{(l)}$

$\Delta H =$ - 171.5 kJ/mol

The oxides may undergo sintering reactions, for which energy was demanded from the source itself.

C. Solidification/Stabilization

The concrete blocks of the varied compositions with Calcined tannery waste, cement, fine aggregate, coarse aggregate; quarry dust were prepared and tested for UCS. . The UCS of concrete blocks prepared with calcined buffing dust was 80 kg/cm^2, calcined chrome shavings was 160 kg/cm^2, calcined primary chemical sludge was 80 kg/cm^2 against the control concrete block 173 kg/cm^2

D. Leachability Studies (TCLP)

The concentrations of COD, TOC and Cr^{3+} in the leachate after 18th hour for the concrete specimen, which has got the highest compressive strength are 58 mg/l, 22 mg/l, 0.5 mg/l for sludge, 66 mg/l, 25 mg/l, 1.1 mg/l for shavings and 64 mg/l, 31 mg/l, 0.51 mg/l. The TCLP study suggests the presence of Cr^{6+} was nil and chromium fixation percentage is calculated using the formula denoted by swarnalatha et al (2006) and it is calculated as 99.11%, 99.95% and 99.99% for sludge, shavings and buffing dust respectively which is considered as the highest value compared. An interesting observation of this study was that Cr^{3+} and COD concentration in the leachate were less than that demanded by the standards (5 mg/l and 280 mg/l for Cr^{3+} and COD respectively) which proved the success of solidifying the incinerated tannery waste (Sollars 1989).

IV. CONCLUSION

The study deals with the starved air Incineration (SAI) of tannery wastes such as sludge, shavings and buffing dust under different oxygen supply (3 g/min, 2.25 g/min & 1.5 g/min) condition at 800C and detailed investigation was carried out for effective utilization of energy without conversion of trivalent chromium to hexavalent chromium. Though net energy change indicates the utilization of the energy in the process, the detailed investigation shows that the energy of the organic fractions are utilized to the maximum extent at the O_2 flow rate of 3.0 g/min. The conversion of trivalent chromium to the hexavalent in the process was nil, which was confirmed by the instrumentation results EPR and FTIR. The calcined waste ash from sludge, shavings and buffing dust were solidified and investigated for the best mode of disposal. The leaching characteristics through TCLP confirmed the effective stabilization of chromium i.e. the metal fixing capacity of different waste ash such as sludge, shavings and buffing dust were 99.11 %, 99.95% and 99.99% respectively.

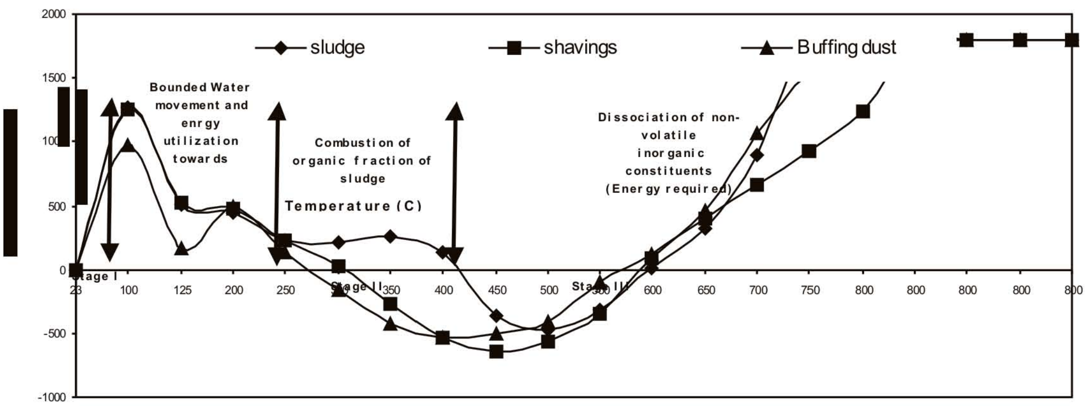

Fig. 2 Effect of Tannery waste for Net energy change (◦ q) with respect to furnace Temperature in correlation with TGA

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