

**Auto Thermal Incineration - Solidification/stabilization for the disposal of primary  
chemical sludge from tanneries**

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**Abstract:**

The high concentration of trivalent chromium along with organic/inorganic compounds in tannery sludge causes severe ground water on land co-disposal and chronic air pollution during incineration. In the present investigation the sludge was subjected to auto-thermal incineration at 800 °C, which prevents the conversion of Cr<sup>3+</sup> to Cr<sup>6+</sup>. The efficiency of Auto thermal incineration was confirmed through instrumental techniques namely TGA, ESR and FTIR. The calcined sludge was solidified/stabilized using different additives fly ash, clay, lime and Portland cement as mixture constituents. The bricks were tested for compressive strength and heavy metal fixation. Compressive strength and metal fixation of the calcined sludge (Cs) – fly ash (F) – cement (C) mortar for the proportion by weight of 41.66% Cs, 41.66% F, 16.66% C were 185 kg/cm<sup>2</sup> and 93.84%, respectively. The stabilization of chromium (III) in the cement gel matrix was confirmed with the Scanning Electron Microscopy. Leachability studies were carried out to determine the percentage of metal fixation and chemical oxygen demand (COD) concentration in the leachate.

**Keywords:** tannery sludge; chromium; auto thermal incineration; fly ash; Portland cement

## INTRODUCTION

In tanneries raw skins/hides are transformed into leather by means of a series of chemical and mechanical operations that leads to discharge of hazardous chemicals into Effluent Treatment Plant (ETP)<sup>1</sup>. Basic Chromium sulphate is the most widely used tanning material for converting putrescible collagen fibres into non-putrescible leather matrix. Only 60% of the chromium salts applied for the tanning process reacts with the raw materials (these Cr<sup>3+</sup> ions are in co-ordination bond with the peptide linkages of collagen fibres of skins/hides). The rest of the chromium salts remains in the exhaust tanning bath and is subsequently discharged into the wastewater<sup>2</sup>.

The dissolved chromium and other spent chemicals, namely proteins, poly phenolic compounds, surfactants, dyes, etc., present in the waste-water are removed through the chemical precipitation technique using lime before the wastewater is allowed to enter the biological treatment process. The precipitated chromium along with the other organic compounds is discharged as sludge<sup>3</sup>.

The current techniques used for the disposal of tannery sludge are land-filling, hydrometallurgical methods to recover chromium, incineration and gasification<sup>4-6</sup>. 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 land-fill sites rapidly reach their total capacity and the authorization of new site becomes difficult<sup>7</sup>. The hydrometallurgical method results in the high cost and poor quality of the chromium due to the presence of organic lipolytic components, metals and other impurities<sup>2,6</sup>. Further more this process is associated with the generation of additional effluent. The investment costs are

far high for gasification; therefore, the total cost is always higher than the incineration and land-filling. But the incineration process has only a total cost of about 1/6 of the total cost for the land-filling scenario<sup>8</sup>. So the thermal incineration is considered as the cheapest alternative and attractive method for its simultaneous energy production and volume reduction of solid waste. Thermal incineration of solid wastes from tanneries needs attention on the issues such as release of toxic chromium(VI), halogenated organic compounds, poly aromatic hydrocarbons, etc., into the environment<sup>9</sup>.

Trivalent chromium is a natural compound of low toxicity, hard to dissolve in water, and hard to be adsorbed by plants. It is an essential micro-nutrient for human beings and other mammals. Trivalent chromium compounds usually exist in the soil as  $\text{Cr}(\text{OH})_3$  or  $\text{Cr}_2\text{O}_3$ . On the other hand, hexavalent chromium is a highly-toxic industrial product, and is soluble in water. It is a carcinogen, which can enter the body via inhalation, ingestion, and contact with the skin. It causes nose bleeding, lung cancer, ulcer, visceral damage, inflamed skin, festering, and even death<sup>10,11</sup>. The incineration temperature and input waste compositions directly affect the formation of Cr(VI) from Cr(III), as does the oxidation–reduction atmosphere in the incineration system. The concentration ratio of chlorine to oxygen at incineration temperatures 900 – 1300 K is an important factor affecting the formation of hexavalent chromium species<sup>12,13</sup>. Attempts have been made to inhibit the formation of these species under the application of a reducing atmosphere. In the present investigation the chemical sludge generated from a garment leather-manufacturing industry was subjected to incineration under the limited oxygen supply (auto thermal incineration), which avoids the conversion of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ . The process produces bottom-ash containing toxic heavy metals 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 of in landfill<sup>14,15</sup>. In the present study the bottom ash was solidified and stabilized in cement-based products containing different mixture components. The focal theme of the present investigation was on (i) assessment of efficiency of auto thermal incineration of tannery sludge (ii) solidification and stabilization (s/s) of bottom ash from the auto thermal incinerator and (iii) leachability studies on the s/s bottom ash.

## **MATERIALS AND METHODS**

### **Chemical and leaching characteristics of tannery sludge**

The primary chemical sludge containing heavy metal chromium (III) was obtained from a physical–chemical ETP, treating wastewater generated from a garment leather manufacturing industry in Chennai. The sludge collected from the settling tank was dewatered in a filter press to 65% of total solids (TS). The dewatered sludge was dried in the laboratory to approximately 95% of TS before use. The dried sludge was pulverized in a ball mill to pass through a screen of size 600  $\mu\text{m}$ . The characterization of the dried sludge such as moisture content, ash content, chemical oxygen demand (COD), polyphenol content, chromium(III) ( $\text{Cr}^{3+}$ ) and chromium(VI) ( $\text{Cr}^{6+}$ ) was determined according to the APHA standard methods<sup>16</sup>. Thermo Gravimetric Analysis (TGA), Electron Spin Resonance (ESR) and Fourier Transformer Infrared (FTIR) studies were carried out to determine thermal stability of sludge, oxidation state of chromium in the sludge and functional groups present in the sludge.

The sludge was subjected to leaching according to American Extraction Procedure Toxicity Test<sup>6</sup>. The procedure consists of using deionized water as extraction medium at different pH (to evaluate the stability of the matrix towards high acidity and alkalinity because the pollutants are highly soluble in acidic and alkaline conditions). The quantity of water was added as 16 times the amount of the sample. The sludge sample with water was agitated for 24 hours. The solid and liquid constituents were separated by filtration and the leachate was characterized chemical oxygen demand (COD), biological oxygen demand (BOD) and poly phenol content. The chromium in the sludge was analyzed using Perkin-Elmer Atomic Absorption Spectroscopy of model 3110 after digestion with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> acid mixture in the ratio of 1:1.

### **Calcination of tannery sludge**

The schematic flow diagram of auto thermal incineration and solidification/stabilization of tannery sludge is shown in figure 1. The incinerator of the size 65.5 × 65.5 × 45.0 cm made up of stainless steel that can hold the maximum capacity of 2 kg of sludge was used for the auto thermal incineration. The dried primary chemical sludge was pulverized in a ball mill to pass through a screen size of 600µm and the pulverized sludge was calcined (prolonged heating at high temperature under oxic environment to drive off moisture and decomposition of sludge) under starved-air condition at 800°C in a vertical type electrical furnace with a provision to collect the ash from the bottom tray and to treat the off gases discharged from the furnace. Auto thermal incineration condition was maintained by flushing with nitrogen in such a way that oxygen concentration was only 10% in the mixture. The oxygen content of N<sub>2</sub>/O<sub>2</sub> mixture for auto thermal incineration was selected such that the increase in the hexavalent chromium in the calcined sludge was nil. The incinerator was designed to operate

the process under controlled reaction temperatures and reaction time using a microprocessor. The partially converted carbon, nitrogen and sulphur compounds in flue gas from the incinerator was further oxidized at 450 °C over Ni-coated ceramic granules (0.05g Ni/g) under the flux of air (30 l/min) in a reactor. The catalytically oxidized flue gas was further scrubbed in a scrubber to remove acidic vapors using alkaline vapours. The bottom ash collected from the incinerator was subjected to TGA, FT-IR and ESR studies.

### **Instrumental Analysis of uncalcined and Calcined Sludge**

#### ***Thermo Gravimetric Analysis:***

Thermo gravimetric Analysis (DTG) was carried out to set the temperature required for calcination of dried and powdered tannery sludge sample under nitrogen atmosphere using Seiko instruments, Japan. The samples were heated in a platinum pan from 40 °C to 800 °C at the rate of 20 °C/min. The mass of the sample used was 2.5 mg.

#### ***FTIR studies:***

Investigation on the functional groups present in tannery sludge was carried out with the help of Perkin-Elmer Fourier Transform Infrared Spectrophotometer (FTIR). The uncalcined and calcined samples were mixed with KBr of spectroscopic grade and pressed into disc of dimensions 10 mm in diameter and 1 mm in thickness. The samples were scanned in the spectral range of 4000–400cm<sup>-1</sup>.

#### ***ESR spectra:***

ESR spectra were recorded on Bruker ESP 300X-band ESR spectrometer at room temperature. Five milligrams of the freeze-dried uncalcined and calcined powdered samples

were placed in a quartz sample tube of 5mm diameter and then subjected to ESR analysis. An X-band microwave with a power of 1 mW and frequency of 9.771 GHz was applied to the specimen.

## **Solidification and stabilization**

### ***Preparation of concrete specimens***

Concrete specimens, measuring  $7.5 \times 5.0 \times 7.5$ , cm were made using 3 mm thick polymethacrylate sheet moulds. The binders used in the study were fly ash (obtained from a thermal foundry, Ennore, Chennai which generates electricity using coal as fuel source), Lime powder (qualigen make), Portland cement 43 grade (Ramco cements, Tamil Nadu) and clay. The fly ash (class F) has the composition of moisture 0.84%, Na<sub>2</sub>O 0.46%, K<sub>2</sub>O 0.85%, MgO 0.31%, CaO 1.13%, Al<sub>2</sub>O<sub>3</sub> 31.3%, SiO<sub>2</sub> 55.92%, Fe<sub>2</sub>O<sub>3</sub> 5.75%, MnO 0.15%, TiO<sub>2</sub> 2.41%, P<sub>2</sub>O<sub>5</sub> 0.88%. The components were mixed (in dry condition) in a mixer until homogeneous mixture was produced. It was made into wet plastic mass using water and again homogenized in an extruder, and casted into moulds. The casted specimens were removed from the moulds after 2 days and cured for 28 days in a constant humidity chamber made of polyacrylic material. The binder to calcined sludge ratio selected to stabilize the heavy metal is shown in Table 2. Unconfined compressive strength (UCS) of the cured concrete specimens was determined in accordance with procedure of ASTM D2850.

### ***Surface Morphology of the Concrete Specimen(SEM-EDX)***

Surface morphology of Calcined Sludge–Fly ash–Cement specimen that has got good compressive strength and metal fixing capacity was examined using Leo-Jeol scanning electron microscopy. The sample was coated with gold by a gold sputtering device for a clear



visibility of the surface morphology. The chemical composition of the hydrated products was analyzed by energy dispersive X-ray (EDX) analysis.

### **Leachability test**

The leachability of the metals from dry sludge and the solidified samples were determined by extraction procedure toxicity test (EPT). The EPT test has been initially used to classify wastes into hazardous and non-hazardous nature. This test is designed to determine semi-volatile organic compounds and heavy metals in tannery sludge; it does not, however, include an analysis of volatile organic compounds. The cured samples were crushed, powdered and homogenized to pass through 9.5 mm screen. The powdered sample of 100 g was taken and placed in a beaker with 1000 ml of deionized water whose pH was adjusted to 6 using 0.1N acetic acid. The contents were agitated in a mechanical shaker at 180 rpm and the liquid phase was separated from the solid phase by filtration through a 0.6–0.8  $\mu\text{m}$  borosilicate glass fiber under pressure of 50 psi (340 KPa). The liquid phase was renewed for every 8 hours and it was analyzed for COD and chromium upto 32 hours.

## **RESULTS AND DISCUSSION**

### **Chemical and leaching characteristics of sludge**

The moisture content, ash content, COD, polyphenol,  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  present in the sludge were 8%, 57%, 524 mg/g, 4.8 mg/g, 2 mg/g and  $<1 \mu\text{g/g}$  respectively. The leachates of primary chemical sludge extracted at different pH (1–11) were characterized by BOD 100–270 mg/l, COD 351–2544 mg/l, poly phenol 44–161 mg/l and  $\text{Cr}^{3+}$  in the range of 0.5–19 mg/l (Table 1). This shows that the tannery chemical sludge contains a considerable amount of organic compounds and heavy metal chromium, which is far higher to discharge onto open land.

## Calcination of tannery sludge

The dried and powdered tannery sludge was incinerated at 800°C under starved supply of oxygen ( $O_2/N_2$  is 0.11). This is to prevent the oxidation of  $Cr^{3+}$  to  $Cr^{6+}$  while maintaining the combustion of organic compounds in the solid waste. The following advantages are expected in starved air combustion:

- Heat recovery from sludge.
- The resulted residue will meet the requirement for solidification and stabilization using Portland cement.
- Ash can be replaced for sand in concrete.
- Disposal volume of sludge is reduced.

Starved air combustion condition was maintained by flushing with nitrogen in such a way that oxygen concentration was only 10% in the mixture. The oxygen content of  $N_2-O_2$  mixture for starved air combustion was selected such that hexavalent chromium in the calcined sludge was nil.

The incineration was carried out at different loadings of sludge (0.5 kg, 1.0 kg & 2.0 kg) and the following terminologies are used in deriving energy balance of starved air combustion:

Heat energy added to the system towards different materials:

Total heat energy of the system  $= q_T$

Heat energy added in heating stainless steel reactor  $= q_1$

Heat energy consumed in heating gas mixture  
 $N_2 - O_2$  entering reactor  $\left. \vphantom{\begin{array}{l} \text{Heat energy consumed in heating gas mixture} \\ \text{N}_2 - \text{O}_2 \text{ entering reactor} \end{array}} \right\} = q_2$

Heat energy lost in circulating water in the  
outer jacket of the lid of the vertical reactor  $\left. \vphantom{\begin{array}{l} \text{Heat energy lost in circulating water in the} \\ \text{outer jacket of the lid of the vertical reactor} \end{array}} \right\} = q_3$

Heat lost during starved air combustion,  $q_N = q_1 + q_2 + q_3$

$$\text{Net heat energy change } (\Delta q) = q_T - q_N$$

where  $q_1, q_2, q_3$  are calculated using  $mc\Delta T$ , where 'm' was the mass of the materials at  $\Delta T$  and 'c' is the specific heat capacity of the materials.

The corresponding net energy change ( $\Delta q$ ) with respect to furnace temperature is shown in Figure 2. It was evident from the energy profile graph that the incineration of sludge involves in three stages, which correlates with the TGA of the sludge.

**Stage – I:**

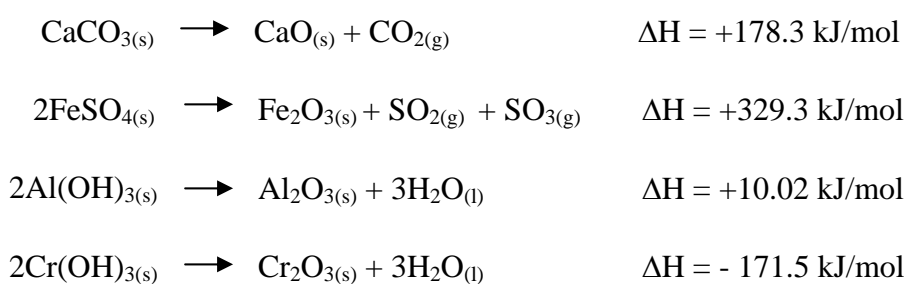
Net heat energy change ( $\Delta q$ ) is positive, which means heat energy was absorbed by the system towards the surface and bound water movement in sludge.

**Stage – II:**

Net heat energy change ( $\Delta q$ ) is negative, heat energy released from the system which can be associated with the combustion of the organic fraction of the sludge.

**Stage – III:**

Net heat energy change ( $\Delta q$ ) is positive, heat energy was absorbed by the system possibly for the decomposition of inorganic compounds such as calcium carbonate (to form calcium oxide), ferrous sulphate (to form ferric oxide), Aluminium hydroxide (to form Alumina), chromium hydroxide (to form chromium oxide) etc. as given below;



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

The total heat energy of the system ( $q_T$ ) in each stage of sludge incineration for the varied sludge loading is presented in Table 2. Although the algebraic sum of  $\Delta q$  for various loading of sludge at various furnace temperature are positive (absorption of the energy by the system), the magnitude of  $\Delta q$  decreased for increased sludge loading i.e., +5.5 kJ/g for sludge

loading of 0.5 kg while it is +1.9 kJ/g for sludge loading of 2kg. This can be illustrated that despite substantial gross calorific value of sludge (9.2 kJ/g), considerable amount of heat energy was expended during incineration due to poor designing of electrical furnace. Thus, the starved air combustion can be made an effective energy recovery process if the following conditions are met:

- High ratio of concentration of organic compounds to inorganic compounds
- Organic compounds with high calorific value in sludge
- Minimization of energy loss ( $q_N$ ) through sound engineering design of incinerator.

Starved air combustion initially suffered operational problems due to the release of volatile organic compounds and partially converted carbon oxides in the flue gas. This was controlled by catalytic combustion of flue gas over nickel impregnated ceramic granules of diameter 7mm (0.05 g of Ni /g of ceramic granule) at 450°C using air as an oxidant. The flue gas from catalytic converter was scrubbed in a scrubber to remove acidic vapors using alkaline water.

### **Thermo Gravimetric Analysis (TGA) of uncalcined and calcined sludge**

DTG of uncalcined sludge (Fig 3a) shows that the weight loss at 96.17 °C is due to elimination of moisture by 10.95%. The elimination of moisture continues upto 280.64 °C, which is due to the loss of the bound water. The organic compounds of tannery sludge such as tannin, synthetic tannin, protein, dye compounds and fatty substances are hydrophilic in nature and thus the water molecules are held in the hydrated form. DTG records a weight loss of 29.14% in the temperature range from 280.64 to 678.3 °C. The weight loss in this

temperature range is due to the decomposition of organic compounds in the uncalcined sludge into intermediate compounds. The intermediate compounds were volatilized off that leaves behind the ash content of 43% in the temperature range from 678 to 731 °C.

The DTG of the calcined sludge was also carried out between 40 and 800 °C (Fig 3b). The objective of this analysis was to select the temperature and duration of calcination. The lower moisture content of calcined sample confirms the decomposition of hydrophilic groups during auto thermal incineration of tannery sludge. However, there exists a weight loss between 223.3 and 520.3 °C, which was due to decomposition of partially burnt organic compounds. The weight loss in the temperature above 520 °C can be attributed to the dehydration of metal hydroxide to metal oxide.

#### **Fourier Transform Infrared Spectroscopy of uncalcined and calcined tannery sludge**

FTIR analysis of the dried uncalcined and calcined sludges was carried out between 400 and 4000  $\text{cm}^{-1}$ . The FTIR spectrum of uncalcined sludge is shown in figure 4a. There is a broad envelope in the higher energy region of 2900 and 3700  $\text{cm}^{-1}$ . The peak centered at 3407.65  $\text{cm}^{-1}$  can be assigned to the overlapping of –OH stretch of water and –NH stretch of the protein group. The intense band lying around 1623.43 and 1550  $\text{cm}^{-1}$  are attributed to the C=O stretching vibration and N–H bending vibration of protein molecule, respectively. The intense peaks at about 873 and 710  $\text{cm}^{-1}$  are attributed to the Cr(III) species.

Figure 4b illustrates the FTIR spectrum of the calcined sample. Medium O–H stretching band centered at 3397.01  $\text{cm}^{-1}$  corresponds to the bound water molecules in the sludge. During calcination of sludge, proteins were converted into amino acids and then into

smaller fragments such as  $\text{NH}_3$  and carboxylate group. The presence of peak at  $1798.3 \text{ cm}^{-1}$  which is assigned to C=O stretching vibration of carboxylate in anhydrite form and  $1138.91 \text{ cm}^{-1}$  corresponding to C–O stretching confirms the calcinations reactions. The absence of alteration in the bands near  $873$  and  $710 \text{ cm}^{-1}$  confirms the conversion of Cr(III) to Cr(VI) did not take place in starved air.

### **Electron Spin Resonance Spectroscopy of uncalcined and calcined sludge**

ESR spectra of uncalcined and calcined sludge are shown in figure 5a & 5b. ESR signal for trivalent chromium (Cr(III)) containing unpaired electron is positive, while Cr(VI) with no unpaired electron shows negative ESR signal. The electronic levels for  $\text{Cr}^{3+}$  ion with its three unpaired electrons gives a total spin  $S = 3/2$  in an octahedral crystal field<sup>17</sup>. The presence of  $\text{Cr}^{3+}$  is exhibited by symmetrical band centered at about  $3480 \text{ G}$  ( $g = 2.046$ ) in both calcined and uncalcined sludge confirms that the conversion of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  was avoided to the maximum extent during auto thermal incineration.

### **Solidification/stabilization**

Solidification and stabilization (s/s) processes are applicable to a wide variety of industrial wastes as a treatment step prior to land-fill disposal. The main goals of s/s are (i) to immobilize the contaminants through chemical and physical mechanisms in order to reduce the rate at which the contaminants can be transferred to the environment and (ii) to enhance the stress–strain properties of processed materials so that they can be utilized in the construction application. The wastes containing heavy metals are stabilized through physical encapsulation, precipitation as a separate phase or uptake by the cement hydration products. During solidification with cement, hydration reactions produce a calcium–silicate–hydrate

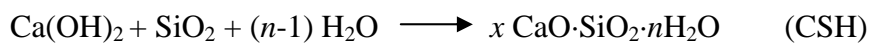
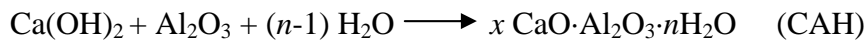
(C–S–H) gel, the particles of C–S–H precipitate out of water onto the silicate-rich layer on the cement grains and gradually form needles or spines known as ettringite (a member of an isostructural group of compounds of prismatic or needle morphology)<sup>18</sup>, the C–S–H and ettringite both plays a major role in binding the heavy metals<sup>19,20</sup>.

### ***Unconfined Compressive Strength (UTS) of calcined sludge specimens***

The concrete specimens of different compositions were prepared and tested for UTS. The values are presented in Table 3. UTS of the mixtures vary with the proportions of the additives. It is observed that the compressive strength increased linearly with the amount of cement in all of compositions.

The addition of clay in the specimens decreases the UTS (47–50.6 kg/cm<sup>2</sup>; S<sub>1</sub>–S<sub>4</sub>), which can be attributed to the fact that the clay contains individual layers of colloidal particles. When these particles were suspended in water, some of these interlayers absorb the positive ions that exist in the specimen leading to expanding these layers. As a result this specimen becomes more elastic as the ratio of clay increases<sup>21</sup>. Replacement of clay by fly ash (F) in the specimens increased the compressive strength significantly. The compressive strength of the cured specimen having the percentage composition of 41.66% Cs, 41.66% F, 16.66% C (S<sub>8</sub>) was about 185 kg/cm<sup>2</sup> which is very near to the requirement of Indian standard for concrete bricks (198.7 kg/cm<sup>2</sup>)<sup>22</sup>. The use of fly ash with Portland cement has many advantages including increased viscosity, preventing phase separation, acting as a pozzolan, binding additional water, decreasing the pore pH and adsorbing metal ions<sup>23,24</sup>.

The concrete specimens that contain both fly ash and lime also possess compressive strength in the order of 150 kg/cm<sup>2</sup>. The presence of lime along with fly ash increases the pH up to 12.8 (pH of the saturated lime water). The solubility of silica and alumina present in the fly ash are greatly increased at this elevated pH levels, making them available for reaction with free calcium from lime and/or fly ash to form cementitious hydrates CAH and CSH, which can be responsible for the compressive strength of the cured specimens.



### ***Surface Morphology***

Hydration of C<sub>3</sub>A in the presence of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) yields ettringite structure (3CaO·Al<sub>2</sub>O<sub>3</sub>·3CaSO<sub>4</sub>·32H<sub>2</sub>O).



The ettringite phase formed favours isomorphous substitution of Al<sup>3+</sup> by Cr<sup>3+</sup>, thus Cr<sup>3+</sup> is immobilized in ettringite crystal inclusion (3CaO·Al<sub>2</sub>O<sub>3</sub>·3CaCrO<sub>4</sub>·32H<sub>2</sub>O) and in bentonite crystal structure (3CaO·Cr<sub>2</sub>O<sub>3</sub>·3CaSO<sub>4</sub>·32H<sub>2</sub>O), which is evident from the scanning electron micrograph of the calcined sludge (Cs)–fly ash (F)–cement (C) specimen (Fig 6).

A graphical representation of EDX showing the composition of various constituents of the solidified blocks is shown in Fig 7. The analysis shows that the principle elements present in an μm-volume region were silicon and calcium. The presence of these elements and their distribution suggest that their sources of the elements may be from C–S–H gel. A



minor amount of  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$  ions was also visible. Thus it confirms that the metals are immobilized in ettringite crystal inclusion.

### Leachability studies

Leaching tests are used to assess: (a) hazardous nature of the waste (b) effectiveness of the solid waste treatment process and (c) suitability of solidified and stabilized solid wastes for land co-disposal.

The concentration of COD and chromium in the leachate collected at eight hourly intervals, for all the concrete specimens are shown in Table 4.

$$\text{Metal Fixation (\%)} = \frac{\left\{ \left[ [\text{Cr}]_{\text{cs}} (W_3 \times W_1 / W_2) \right] - [\text{Cr}]_{\text{L}} \right\}}{\left[ [\text{Cr}]_{\text{cs}} (W_3 \times W_1 / W_2) \right]} \times 100$$

where  $[\text{Cr}]_{\text{cs}}$  = concentration of chromium present in the calcined sludge

$W_1$  = dry weight of calcined sludge in the specimen

$W_2$  = Total weight of a solidified specimen

$W_3$  = Weight of a solidified specimen taken for the leaching test

$[\text{Cr}]_{\text{L}}$  = concentration of chromium in the leachate

The percentages of metal fixation are shown in Table 3. For each composition, as the ratio of cement was increased the metal fixation efficiency was increased and the COD concentration was decreased in the leachate. The ettringite structure formed from the hydration product of cement stabilizes chromium. A cement-based s/s product provides a dense physical matrix of low permeability, which constitutes a physical barrier to leaching<sup>25</sup>.

In limestone-blended cement, the incorporation of  $\text{CO}_3^{2-}$  to the system must be considered. Hydrated calcium aluminate becomes carboaluminates, probably for the exchange of  $\text{OH}^-$ . The presence of chromium retards the formation of carboaluminates in limestone–Portland cement hydration, especially at early ages<sup>26</sup>.

The concrete specimens containing clay and fly ash show the good metal fixing capacity (86–94%) and also low COD concentration in leachate (maximum concentration was 96 mg/l in Cs–Cy–C type and 90 mg/l in Cs–F–C type). Apart from the ion-replacement mechanism, the introduction of fly ash will decrease the C/S ratio of C–S–H and increase the retention of cationic contaminants in C–S–H. And also the presence of fly ash decreases or eliminates the free lime content in hardened cement pastes, thus it refines the pore structure of the paste and reduce the permeability of hardened pastes<sup>25,27</sup>. It is also expected that  $\text{Cr}^{3+}$  be effectively immobilized at high pH due to the precipitation into insoluble chromium hydroxide. The metal fixation ability of clay containing specimens was comparable with fly ash included specimens. The addition of clay to the specimen, however, plays a role of enhancing the liquid limit and plasticity index. Thus more micro and macro pores will be opened to improve more ion exchange on the active sites of the sample<sup>21</sup>. And also be due to the fact that the addition of clay in the mixture reduces available water and increases viscosity, which makes good sorption towards organic compounds and heavy metals<sup>28</sup>. Among the combinations tried, the inclusion of lime in the mixture showed the maximum chromium concentration of 2050  $\mu\text{g/l}$  in the leachate. The reaction becomes slower in addition of lime and thus results in a different kind of pozzolanic<sup>26</sup> reaction. Lime has a pH of approximately 12.4 at room temperature. The presence of highly soluble alkaline salts, common in cement and wastes, suppresses the dissolution of  $\text{Ca}(\text{OH})_2$  and elevates pore

water pH towards a value of 14. Because of this unfavorable pH condition the solubility of the metal and organics were maximum<sup>25,29</sup>. Thus the lime based system decreases the metal fixation by 37% and increases the concentration of COD in the leachate to 240 mg/l. An interesting observation of this study was that Cr<sup>3+</sup> and COD concentration in the leachate were less than that demanded by the USEPA standards<sup>30</sup> (5 mg/l and 280 mg/l for Cr<sup>3+</sup> and COD, respectively) which has proved the success of solidifying the incinerated waste.

Auto thermal incineration, followed by s/s using fly ash appears to be a cost effective system because in this system the conversion of Cr<sup>3+</sup> to Cr<sup>6+</sup> is avoided just by controlling the oxygen concentration in the mixture without the addition of any reducing agent. More input of air can lead to the loss of heat (high energy consumption) and also leads to the formation of toxic Cr(VI) species. If the energy consumption encountered in the system (Auto thermal incineration) were made equal to the energy released by the solid waste, the system would become more cost effective.

## CONCLUSIONS

Auto thermal incineration of tannery sludge under starved-air (N<sub>2</sub>:O<sub>2</sub> – 90:10) condition at 800 °C and followed by catalytic combustion over Ni coated ceramic granules at 450 °C were the initial steps before solidification/stabilization. The ESR analysis of calcined sludge showed that Cr<sup>3+</sup> in the tannery sludge was not converted into Cr<sup>6+</sup> during auto thermal incineration at 800 °C. The bottom ash was solidified/stabilized using Portland cement, fly ash, clay and lime as primary binders. Among the combinations, calcined sludge (Cs): fly ash (F): cement (C) at the ratio of 41.66%, 41.66%, 16.66% has yielded the concrete specimen of compressive strength 185 kg/cm<sup>2</sup> and metal fixation capacity of 93.84%. The compressive strengths of the solidified samples varied with the proportions of the different components

added to the mixture. The addition of fly ash along with cement increased compressive strength of the cured specimen. Fly ash also improved the metal fixing capacity of ettringite gel structure formed during solidification. Scanning Electron Microcopy confirmed the formation of ettringite gel structure during solidification, which stabilized Cr (III) through isomorphous inclusion in the microstructure. The metal fixing efficiency of specimens containing clay was appreciably good but possesses very poor compressive strength. In the presence of lime, the compressive strength was fairly good but metal fixing capacity was not satisfied. The concentration of COD and  $\text{Cr}^{3+}$  present in the leachate were well below the standards prescribed.

The study concludes that the organic fractions of tannery sludge can be destructed using auto thermal incineration, which avoids the formation of hexavalent chromium. And the resultant bottom ash (calcined sludge, Cs) comprises of residual organics and metal oxides can be solidified and stabilized using the combination of cement (C) and fly ash (F) mixture along with the additives, and can be used as a constructional material.

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**Table – 1. Characteristics of leachate of tannery sludge at different pH conditions**

<b>S. No.</b>	<b>pH condition</b>	<b>BOD (mg/l)</b>	<b>COD (mg/l)</b>	<b>Polyphenol (mg/l)</b>	<b>Chromium (mg/l)</b>
1	1	270	1096	161	19
2	2	230	547	95	17
3	3	225	509	60	9
4	4	210	474	60	2
5	5	120	435	60	1
6	6	100	360	44	1
7	7	100	351	44	1
8	8	110	491	51	0.5
9	9	195	500	52	1
10	10	230	535	53	2
11	11	240	2544	92	2



**Table 2. Total energy consumed ( $q_T$ ) for incineration in the temperature range of ambient - 800°C at various loading rate of sludge**

Raise in temp. (°C)	Total energy in kJ ( $q_T$ )		
	0.5 kg	1.0 kg	2.0 kg
41.8 – 99.8	1044	891.9	126.21
99.8 – 200.0	1044	732.0	343.5
200.0 – 216.7	1515	1261.2	416.9
216.7 – 303.3	1800	1103.2	874.1
303.3 – 366.8	864	802.9	687.8
366.8 – 391.7	432	441.4	359.7
391.7 – 400.0	504	466.4	331.5
400.0 – 450.1	1238.1	1044	909
450.1 – 466.6	1313.2	1044	725.6
466.6 – 500.0	1444.7	1432.6	1251.3
500.0 – 516.7	1541.0	1439.6	1358.9
516.7 – 600.0	2229.0	2130.7	1834.9
600.0 – 678.5	2628.2	2744.8	3206.1
678.5 – 750.1	3078.2	4103.6	4157.7
750.1 – 800.0	2983.8	3974.1	5122.2
800.0 – 800.0	2520	3132	3488
800.0 – 800.0	3132	3212	3600
800.0 – 800.0	1980	2808	2900
800.0 – 800.0	1044	1404	1800
$\Sigma q_T$	32,335.0	34,168.2	33,493.4
$\Sigma q_N$	29,583.6	29,627.7	29,716.1
$\Delta q (\Sigma q_T - \Sigma q_N)$	+ 5.5 kJ/g	+ 4.5 kJ/g	+ 1.9 kJ/g

$\Sigma q_T$  = Sum of  $q_T$

$\Sigma q_N$  = Sum of  $q_N$  ;  $q_N = q_1 + q_2 + q_3$

**Table – 3. Percentage composition of concrete blocks, their respective compressive strength and the percentage of metal fixation**

<b>Sample No.</b>	<b>Percentage composition (%)</b>	<b>Compressive Strength (kg/cm<sup>2</sup>)</b>	<b>Metal Fixation (%)</b>
S <sub>1</sub>	44.44% Cs, 44.44% Cy, 11.11% C	47.24	86.12
S <sub>2</sub>	43.5% Cs, 43.5 % Cy, 13.0% C	50.08	89.04
S <sub>3</sub>	42.5 % Cs, 42.5% Cy, 15 % C	50.26	91.30
S <sub>4</sub>	41.66 % Cs, 41.66 % Cy, 16.66 % C	50.60	93.42
S <sub>5</sub>	44.44% Cs, 44.44 % F, 11.11% C	63.77	86.12
S <sub>6</sub>	43.5 % Cs, 43.5 % F, 13% C	89.28	89.03
S <sub>7</sub>	42.55 % Cs, 42.55 % F, 14.5% C	172.19	92.02
S <sub>8</sub>	41.66 %Cs, 41.66% F, 16.66% C	184.9	93.84
S <sub>9</sub>	40 % Cs, 40 % F, 10 % L, 10% C	112	81.87
S <sub>10</sub>	38.5 % Cs, 38.5 % F, 11.5 % L, 11.5 %C,	143.4	86.13
S <sub>11</sub>	37.0 % Cs, 37.0% F, 13.0 % L, 13.0 % C	146	89.16
S <sub>12</sub>	35.7 % Cs, 35.7% F, 14.29% L, 14.29% C,	150	92.06
S <sub>13</sub>	46.5 % Cs, 23.25% F, 23.25% Cy, 7.0% C	42.5	74.71
S <sub>14</sub>	45.5 % Cs, 22.73 % F, 22.73% Cy, 9.0 %C	51.0	84.3
S <sub>15</sub>	44.4% Cs, 22.2% F, 22.2 % Cy, 11.11% C	56.68	88.22
S <sub>16</sub>	43.5 % Cs, 21.75 % F, 21.75% Cy, 13% C	59.5	90.32
S <sub>17</sub>	43.5 %Cs, 21.75% F, 21.75% Cy, 6.5% C, 6.5% L	105.2	62.65
S <sub>18</sub>	41.7% Cs, 20.8% F, 20.8% Cy, 8.3% C, 8.3% L	108.4	73.14
S <sub>19</sub>	40 % Cs, 20% F, 20% Cy, 10% C, 10% L	114.7	81.4
S <sub>20</sub>	38.5% Cs, 19.23% F, 19.23% Cy, 11.5% C, 11.5 % L	116.6	87.07

C<sub>s</sub> - Calcined Sludge; F - Flyash ; Cy - Clay; C - Cement; L - Lime

**Table – 4. The Concentration of Chemical Oxygen Demand (COD) and Chromium (III) present in the leachate of cured concrete specimens**

Sample No.	COD concentration, mg/l				Chromium (III) concentration, µg/l			
	8 <sup>th</sup> hr	16 <sup>th</sup> hr	24 <sup>th</sup> hr	32 <sup>nd</sup> hr	8 <sup>th</sup> hr	16 <sup>th</sup> hr	24 <sup>th</sup> hr	32 <sup>nd</sup> hr
S <sub>1</sub>	96	81	62	60	750	520	400	380
S <sub>2</sub>	90	65	52	47	630	410	320	300
S <sub>3</sub>	71	58	43	30	500	320	250	220
S <sub>4</sub>	55	39	27	26	420	220	190	170
S <sub>5</sub>	90	70	58	52	750	500	410	375
S <sub>6</sub>	80	58	41	38	625	410	330	290
S <sub>7</sub>	60	40	37	19	475	300	235	205
S <sub>8</sub>	50	31	17	15	350	185	140	120
S <sub>9</sub>	240	180	150	125	1150	800	555	475
S <sub>10</sub>	190	125	100	80	925	625	375	360
S <sub>11</sub>	160	100	80	65	800	425	325	300
S <sub>12</sub>	135	93	55	40	650	380	310	265
S <sub>13</sub>	92	84	62	54	1250	650	550	400
S <sub>14</sub>	85	65	52	43	775	550	300	150
S <sub>15</sub>	68	58	45	29	650	350	175	100
S <sub>16</sub>	53	34	25	20	550	300	160	50
S <sub>17</sub>	235	180	143	120	2050	1350	750	450
S <sub>18</sub>	160	111	89	80	1550	780	360	350
S <sub>19</sub>	127	91	71	60	750	400	305	285
S <sub>20</sub>	120	88	53	38	600	300	270	235

