

Starved air combustion–solidification/stabilization of primary chemical sludge from a tannery

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Abstract

The high concentration of trivalent chromium along with organic/inorganic compounds in tannery sludge causes severe ground water contamination in the case of land disposal and chronic air pollution during incineration. In the present investigation, the sludge was subjected to flow-through column test to evaluate the concentration of leachable organics (tannin, COD and TOC) and heavy metal ions (Cr^{3+} , Fe^{2+}) present in it. The dried sludge was incinerated at 800°C in an incinerator under starved oxygen supply (starved-air combustion) to prevent the conversion of Cr^{3+} to Cr^{6+} . The efficiency of starved air combustion was studied under different loading rates of sludge. The calcined sludge was solidified/stabilized using fly ash and Portland cement/gypsum. The solidified bricks were tested for unconfined compressive strength and heavy metal leaching. Unconfined compressive strength of the blocks was in the range of $83\text{--}156\text{ kg/cm}^2$. The stabilization of chromium (III) in the cement gel matrix was confirmed with scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDX). Leachability studies on solidified bricks were carried out to determine the metal fixation and dissolved organic (as COD) concentration in the leachate.

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1. Introduction

In tanneries raw skins/hides are transformed into leather by means of a series of chemical and mechanical operations that lead to discharge of hazardous chemicals into effluent treatment plant (ETP) [1]. Basic chromium sulfate 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 react with the raw materials (Cr^{3+} ions are in co-ordination bond with the peptide linkages of collagen fibres of skins/hides) while rest of the chromium salts remain in the exhaust tanning bath and they are subsequently discharged into the wastewater [2].

The dissolved chromium and other spent chemicals, namely proteins, poly phenolic compounds, surfactants, dyes, etc. present in the wastewater 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 [3].

The techniques such as land co-disposal, thermal treatment and anaerobic digestion are practiced for the disposal of solid wastes discharged from ETP [4]. The solid waste disposal is considered to be efficient if the energy involved is balanced in the overall recycle process. This balancing of energy supply and demand is a key concept in creating an efficient recycling-based processes [5].

The most competitive technologies for energy recovery from discharged sludge are land filling, incineration, and gasification [6,7]. Land-filling scenario faces the highest cost, which is explained by the combination of the overall high pollution emissions and low energy recovery. The investment costs are far high for gasification, therefore, the total cost is always higher than for incineration and land filling. But cost of the thermal incineration process is only about 1/6th of the total cost for the land filling scenario [8]. And also the available landfill sites rapidly reach their total capacity and the authorization for new sites becomes difficult [9]. So the thermal incineration is considered as the cheapest alternative and attractive method for its simultaneous energy production and volume reduction of solid

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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 [10].

The major species formed from Cr (III) during thermal incineration of solid waste are $\text{Cr}_2(\text{SO}_4)_3(\text{s})$, $\text{CrOCl}_2(\text{g})$ and $\text{Cr}_2\text{O}_3(\text{s})$ which later accounts a path for the formation of Cr (VI) [11,12]. Solid waste composition and oxygen concentration in the incinerator determine the extent of conversion of Cr^{3+} to Cr^{6+} . Attempts have been made to inhibit the formation of these species under the supply of reduced oxygen atmosphere. Starved air combustion is a process, in which wastage of energy is minimum. In the present investigation, the primary chemical sludge generated from a garment leather manufacturing industry is subjected to starved air combustion to increase its efficiency through energy recovery. Adequate care was taken to avoid the conversion of Cr^{3+} to Cr^{6+} during thermal incineration. 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 off as landfill [13,14]. In the present study the bottom ash was solidified and stabilized using Portland cement/gypsum with fly ash and different additive mixtures. The focal theme of the present investigation was on (i) optimizing the efficiency of the starved air combustion of tannery sludge through energy balance, (ii) solidification and stabilization (s/s) of bottom ash produced from the auto thermal incinerator, and (iii) leachability studies on the s/s bottom ash.

2. Materials and methods

2.1. Chemical and leachate characteristics of tannery sludge

The primary chemical sludge containing heavy metal chromium (III) was obtained from a physical–chemical ETP of 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 to approximately 95% of TS. The dried sludge was pulverized in a ball mill to pass through a screen of size 600 μm . The characterization of the dried sludge such as moisture content, ash content, chemical oxygen demand (COD), total organic carbon (TOC), tannin, chromium (III), and ferrous ion (Fe^{2+}) was determined according to the APHA standard methods [15]. Thermogravimetric analysis (TGA) and Fourier transformer infrared (FT-IR) studies were carried out to determine thermal stability of sludge and functional groups present in the sludge respectively.

The sludge was subjected to packed bed flow-through leaching test, which was used to determine the rate of contaminant release during advective mass transport and to infer primary release mechanism. In the vertical column of inner diameter 2.5 cm and the height 40 cm, the sludge was packed to different bed depths of 7 (36 g), 14 (72 g) and 21 (108 g) cm. The deionized water was used as extraction medium at pH 4.7 (adjusted using

0.01 M acetic acid) and pH 10 (adjusted using 1 M sodium carbonate). Aliquots of samples from the outlet of the column were collected and analyzed for COD, TOC, tannin, Cr^{3+} and Fe^{2+} ion. The column breakthrough time (for 90% removal, denoted as $t_{90\%}$) was determined for the above bed depths with different flow rates of 1, 5 and 10 ml/min.

2.2. Starved air combustion of chemical sludge

The schematic flow diagram of starved air combustion and solidification/stabilization of tannery sludge is shown in Fig. 1. The dried primary chemical sludge was pulverized in a ball mill to pass through a screen of size 600 μm and the pulverized sludge was loaded in a stainless steel (316 grade) vertical reactor of weight 13 kg, which was placed in an electrical furnace. The sludge was 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 (5 l/min) with a gradual increase in temperature at five segments for about 9 h.

Segment I: Ambient temperature \rightarrow 300 °C (rate of heating 270 °C h⁻¹).

Segment II: 300 °C \rightarrow 500 °C (rate of heating 50 °C h⁻¹).

Segment III: 500 °C \rightarrow 600 °C (rate of heating 100 °C h⁻¹).

Segment IV: 600 °C \rightarrow 800 °C (rate of heating 200 °C h⁻¹).

Segment V: 800 °C \rightarrow 800 °C (soaking for 2 h).

The flushing of the gas mixture was stopped in the last segment to avoid the conversion of Cr^{3+} to hexavalent chromium (Cr^{6+}). The outer jacket of the lid of the heating vessel was circulated with cool water (at temperature 30 °C) at a flow rate of 0.5 l/min for condensing volatile organic compounds back into incinerator. The incinerator was designed to operate the process under controlled reaction temperatures and reaction time using a microprocessor. 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 weights of the dried sludge (0.5, 1.0 and 2.0 kg) 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 of 1 m height and 17.5 cm diameter to remove acidic vapors using alkaline water. The flue gas free from acidic vapors was further oxidized at 450 °C over Ni-coated ceramic granules (0.05 g of Ni/g) under the flux of air (30 l/min) in a separate reactor to convert hydrocarbon and carbon monoxide to stable end products. The bottom ash collected from the incinerator was subjected to TGA and FT-IR studies.

2.3. Solidification and stabilization

2.3.1. Preparation of concrete blocks

Both the cold and hydraulic molding were used to prepare the solidified concrete blocks. Concrete blocks, measuring 8 cm \times 6 cm \times 5 cm was made using 3 mm thick

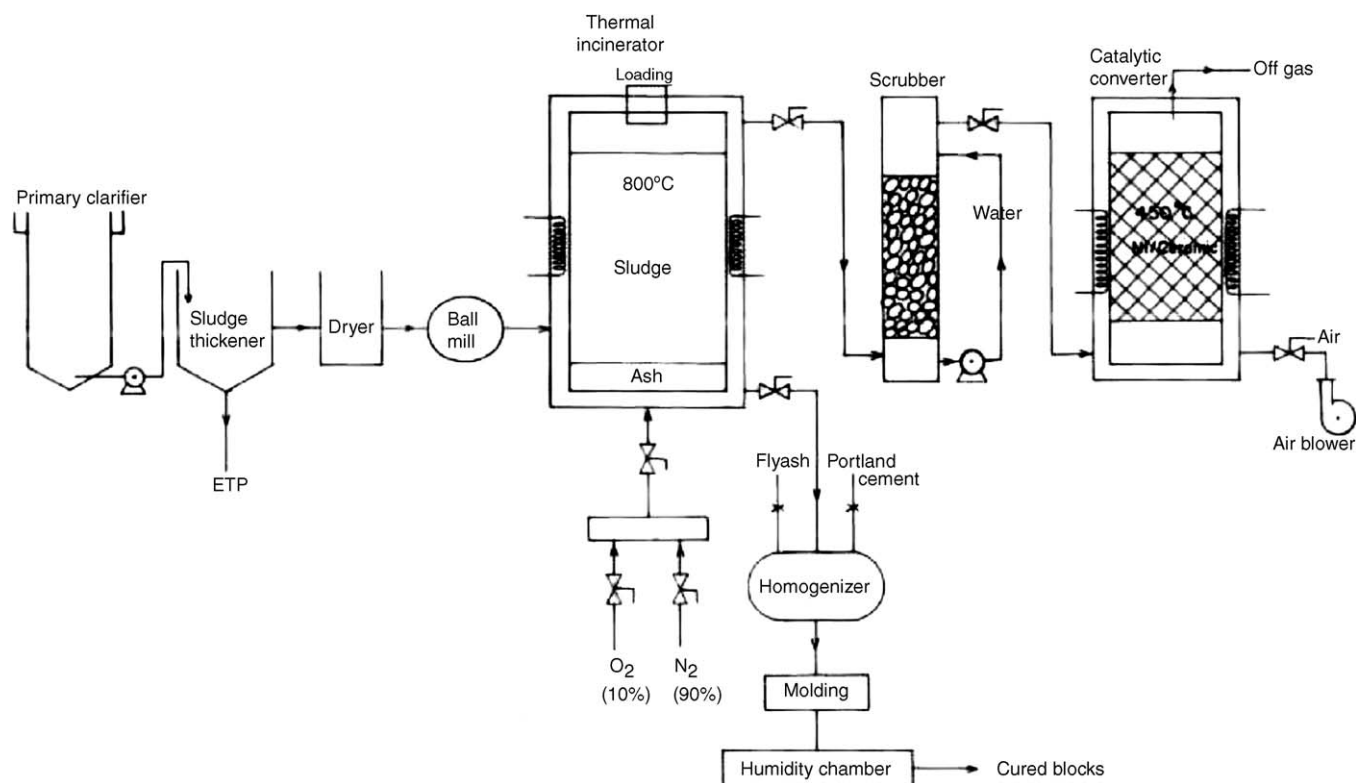


Fig. 1. Starved air combustion and solidification/stabilization system for sludge discharged from a leather manufacturing industry.

polymethacrylate sheet for cold molding and the same size of mild steel sheets were used for hydraulic molding. Fly ash obtained from a thermal foundry, Chennai, was used as one of the binders for making concrete molds. The fly ash has the composition as follows: moisture 0.84%, Na_2O 0.46%, K_2O 0.85%, MgO 0.31%, CaO 1.13%, Al_2O_3 31.3%, SiO_2 55.92%, Fe_2O_3 5.75%, MnO 0.15%, TiO_2 2.41%, P_2O_5 0.88%. Portland cement 43 grade (RAMCO Cements, Tamil Nadu) and gypsum were also used as binders for solidification of bottom ash because of their cheapness and availability. The three components namely calcined sludge, fly ash, and Portland cement/gypsum were mixed (in dry condition) in equal proportions to get the total quantity of 330 g in a homogenizer until 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. For hydraulic molding the blocks were maintained at a hydraulic pressure of 900 Kg/cm^2 for about 1 min. Then, the blocks were separated from molds and cured in constant humidity chamber. Unconfined compressive strength (UCS) of the cured concrete blocks was determined in accordance with the procedure of ASTM D2850.

2.3.2. Instrumental analysis of uncalcined, calcined sludge and solidified bricks

2.3.2.1. TGA. TGA was carried out to determine the weight loss with respect to temperature. The dried and powdered samples were analyzed under nitrogen atmosphere using Seiko Instruments (Japan). The samples were heated in a platinum pan from

40 to 800 $^\circ\text{C}$ at the rate of 20 $^\circ\text{C}/\text{min}$. The mass of the sample used was 2.5 mg.

2.3.2.2. FT-IR studies. Investigation on the functional groups present in the samples was carried out with the help of FT-IR (Perkin-Elmer spectrophotometer). The uncalcined and calcined samples were mixed with KBr of spectroscopic grade and pressed into disk of dimensions 10 mm in diameter and 1 mm in thickness. The samples were scanned in the spectral range of 400–4000 cm^{-1} .

2.3.2.3. Surface morphology of the concrete block (SEM-EDX). Surface morphology of calcined sludge–fly ash–cement/gypsum brick was examined using Leica Stereo Sean 440 scanning electron microscopy (SEM). 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.

2.4. Leachability test

The leachability of metals and organics (as COD) from dry sludge and the solidified samples were determined by extraction procedure test (EPT). The EPT has been 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 the analysis of volatile organic compounds. The cured samples were crushed, powdered, homogenized (greater the surface area, more is the leachability) [16,17] to pass through 5 mm

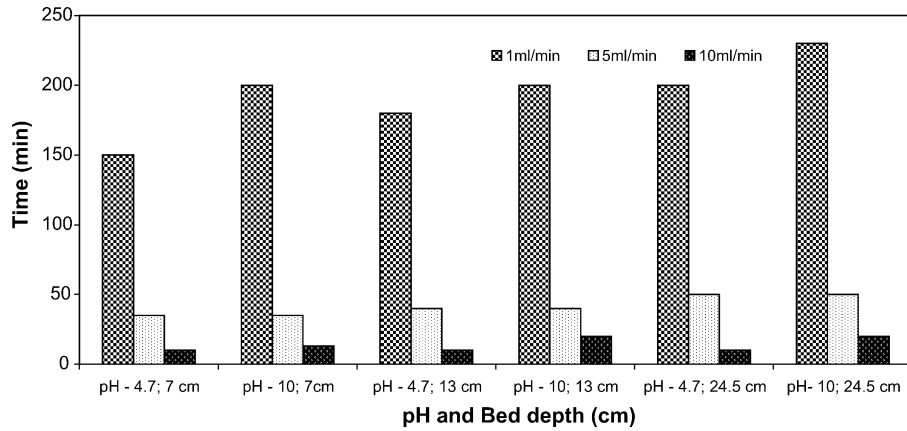


Fig. 2. Breakthrough time ($t_{90\%}$) for leaching of TOC in the sludge at various bed depth and flow rate.

screen. The powdered sample of weight 50 g was placed in a beaker with 1000 ml of deionized water whose pH was adjusted to 5 using 0.1 N 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 μm borosilicate glass fiber under pressure of 50 psi (340 KPa). The liquid phase was renewed for every 24 h (50 ml) and it was analyzed for COD, ferrous ion and chromium ion up to 7 days.

3. Results and discussion

3.1. Leaching characteristics of sludge

The moisture content, ash content, COD, TOC, tannin, Cr^{3+} and Fe^{2+} of the sludge were 8%, 57%, 524, 61, 4.8, 11 and 6 mg/g, respectively. The ratio (C_t/C_0) of the leachate concentration at any time to the initial leachate (for TOC, COD, tannin, Cr^{3+} and Fe^{2+}) concentration was plotted against time at pH 4.7 and at pH 10 for various flow rates 1, 5 and 10 ml/min at different bed depths of 7, 13 and 24.5 cm. The breakthrough time ($t_{90\%}$) was calculated from the break through curves. The $t_{90\%}$ values for the removal of various pollutants and for different bed depths are presented in Figs. 2–6.

The contact time of sludge with leachate in the column plays a major role in determining the breakthrough time. The breakthrough time was increased with increase in column depth (h) and decreased with flow rate (Q) ($t_{90\%} \propto h/Q$). The pH of the leachant is also considered to be an important parameter. In the alkaline pH range, the quantity of pollutant release is influenced by (i) complexation of dissolved organic content with chelants, (ii) reduction or oxidation of constituents to form metal hydroxides, or (iii) adsorption on mineral surfaces. Thus, the breakthrough time was higher at pH 10 than the same at pH 4.7.

3.2. Starved air combustion 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.

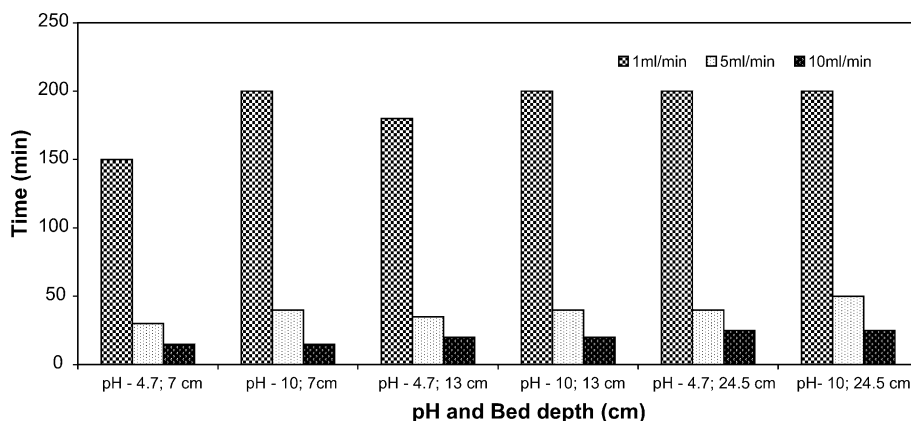


Fig. 3. Breakthrough time ($t_{90\%}$) for leaching of COD in the sludge at various bed depth and flow rate.

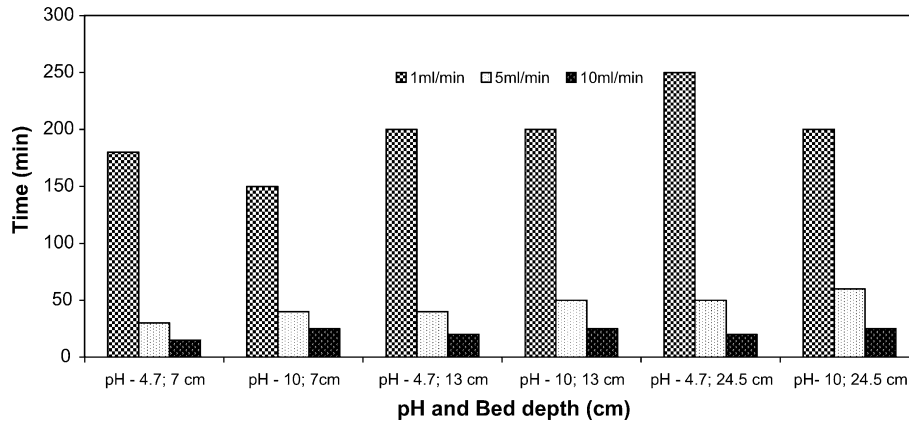


Fig. 4. Breakthrough time ($t_{90\%}$) for leaching of tannin in the sludge at various bed depth and flow rate.

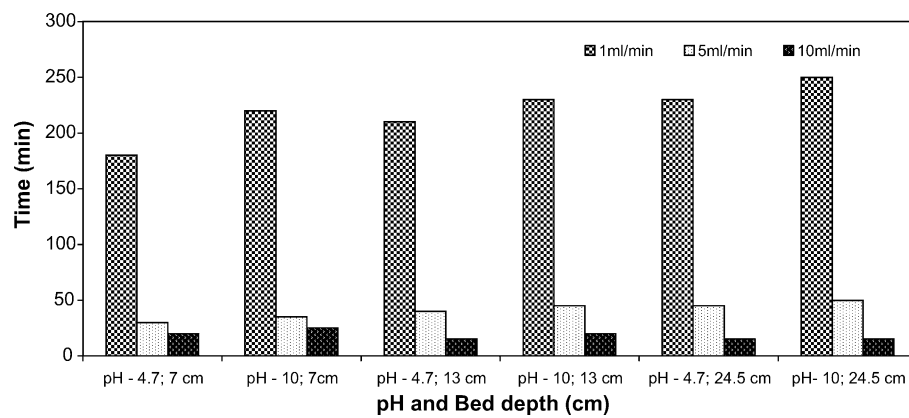


Fig. 5. Breakthrough time ($t_{90\%}$) for leaching of chromium (III) in the sludge at various bed depth and flow rate.

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 N₂–O₂ 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, 1.0 and 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:

$$\text{total heat energy of the system} = q_T$$

$$\text{heat energy added in heating stainless steel reactor} = q_1$$

$$\text{heat energy consumed in heating gas mixture N}_2\text{–O}_2$$

$$\text{entering reactor} = q_2$$

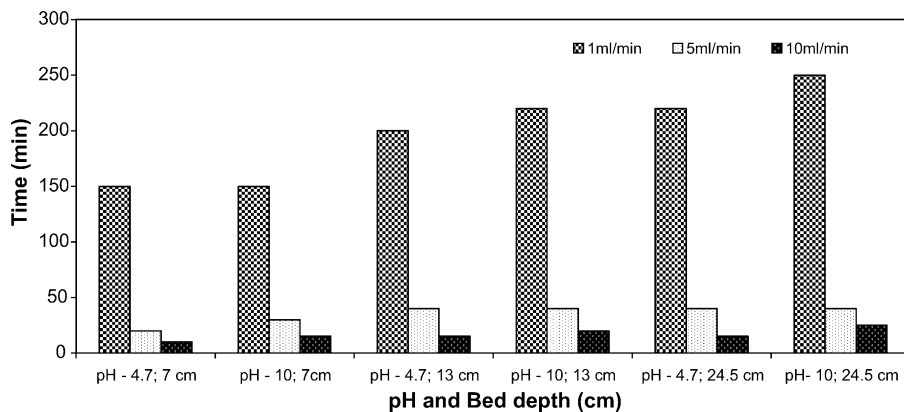


Fig. 6. Breakthrough time ($t_{90\%}$) for leaching of ferrous in the sludge at various bed depth and flow rate.

heat energy lost in circulating water in the outer jacket of the lid of the vertical reactor = q_3

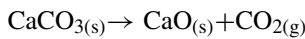
heat lost during starved air combustion, $q_N = q_1 + q_2 + q_3$

net heat energy change (Δq) = $q_T - q_N$

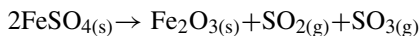
where q_1, q_2, q_3 are calculated using $mc\Delta T$, where 'm' was the mass of the materials at ΔT and 'c' is the specific heat capacity of the materials.

The corresponding net energy change (Δq) with respect to furnace temperature is shown in Fig. 7. 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 (Δq) 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 (Δq) 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 (Δq) 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;



$$\Delta H = +178.3 \text{ kJ/mol}$$



$$\Delta H = +329.3 \text{ kJ/mol}$$



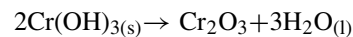
$$\Delta H = +10.02 \text{ kJ/mol}$$

Table 1

Total energy consumed (q_T) for incineration in the temperature range of ambient–800 °C at various loading rate of sludge

Raise in temperature (°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
Σq_T	32335.0	34168.2	33493.4
Σq_N	29583.6	29627.7	29716.1
$\Delta q (\Sigma q_T - \Sigma q_N)$	+5.5 kJ/g	+4.5 kJ/g	+1.9 kJ/g

Σq_T = sum of q_T ; Σq_N = sum of q_N ; $q_N = q_1 + q_2 + q_3$.



$$\Delta H = -171.5 \text{ kJ/mol}$$

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 1. Although the algebraic sum of Δq for various loading of sludge at various furnace temperature are positive (absorption of the energy by the system), the magnitude of Δq decreased

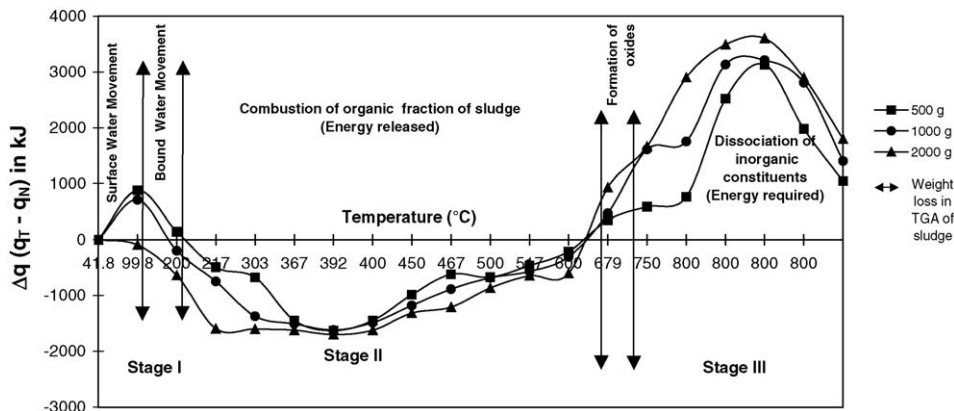


Fig. 7. Net energy change (Δq) with respect to furnace temperature for various loading rate of sludge correlated with TGA.

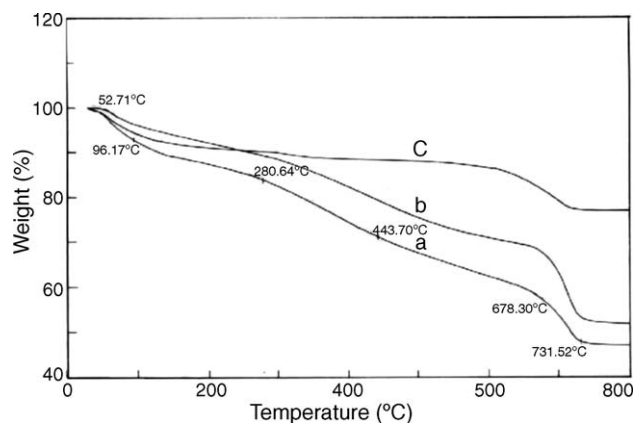


Fig. 8. TGA spectrum of (a) uncalcined sludge, (b) calcined sludge and (c) solidified blocks.

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 2 kg. 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 7 mm (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.

3.3. Instrumental analysis of uncalcined and calcined sludge

3.3.1. TGA

TGA of uncalcined sludge (Fig. 8a) 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 bound form. TGA records a weight loss of 29.14% in the temperature range from 280.64 to 678.3 °C, which can be attributed to the decomposition of organic compounds in the uncalcined sludge into intermediate compounds. The intermediate compounds were volatilized off that left behind the ash content of 43% in the temperature range from 678 to 731 °C.

The thermo gravimetric analysis of the calcined sludge was also carried out in the temperature range between 40 and 800 °C (Fig. 8b). 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 starved air combustion of tannery sludge. However, there exists a weight loss between 223.3 and 520.3 °C, which can be due to decomposition of partially burnt organic compounds. The weight loss in the temperature above 520 °C can be attributed to dehydration of metal hydroxide to metal oxide.

3.3.2. FT-IR

FT-IR analysis of the dried uncalcined and calcined sludges was carried out in the frequency range between 400 and 4000 cm^{-1} . The FT-IR spectrum of uncalcined sludge is shown in Fig. 9a. There is a broad envelope in the higher energy region 2900 and 3700 cm^{-1} . The peak centered at 3407.65 cm^{-1} can be assigned to overlapping of –OH stretch of water and –NH stretch of protein group. The intense band lying around 1623.43 and 1550 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 cm^{-1} are attributed to the Cr (III) species.

Fig. 9b illustrates the FT-IR spectrum of the calcined sample. There is only a medium O–H stretching band centered at 3397.01 cm^{-1} corresponding to the bound water molecules in the sludge. During calcination of sludge, proteins are converted

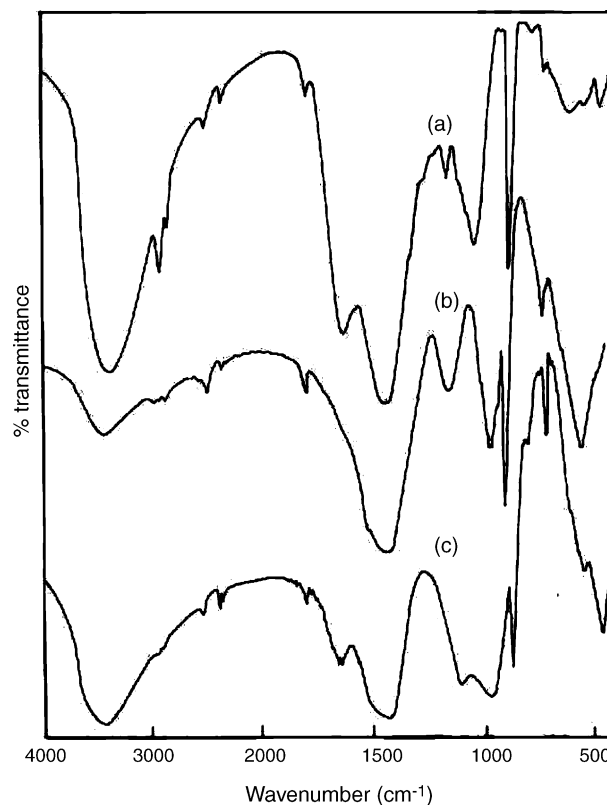


Fig. 9. FT-IR spectrum of (a) uncalcined sludge, (b) calcined sludge and (c) solidified blocks.

Table 2
Unconfined compressive strength of the solidified blocks

Composition of the block	Compressive Strength (kg/cm ²)
Cold moulding	
Calcined sludge–cement–flyash (Cs–C–F)	145.83
Calcined sludge–gypsum–flyash (Cs–G–F)	83.33
Hydraulic moulding	
Calcined sludge–cement–flyash (Cs–C–F)	156.24
Calcined sludge–gypsum–flyash (Cs–G–F)	98.96

into amino acids and then into smaller fragments such as NH₃ and carboxylate group. These conversions are showed by peak at 1798.3 cm⁻¹ which is assigned to C=O stretching vibration of carboxylate in anhydride form and its corresponding C–O stretching is observed as shoulder peak at 1138.91 cm⁻¹. Absence of alteration in the bands near 873 and 710 cm⁻¹ confirm the absence of Cr (III) to Cr (VI) conversion in auto thermal incinerator. The presence of hydrated monocalcium aluminate is assigned in FT-IR by the typical band CO₃²⁻ split at 1423.22 cm⁻¹ and a shoulder at 1066 cm⁻¹.

3.4. Solidification/stabilization

Solidification and stabilization (s/s) processes are applicable to a wide variety of industrial wastes as a treatment step prior to long-term storage on land. 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 transported to the environment and (ii) to increase the structural integrity of the treated material. Wastes containing heavy metals are often treated with alkaline and cementing agents to precipitate the metal ions in free form and to yield a solid matrix of desirable strength. During solidification with Portland cement, hydration reaction produces a calcium–silicate–hydrate (C–S–H) gel representing a meta stable precursor of crystalline phases such as tobermorite and jennite. These phases and the formation of ettringite are responsible for creating filamentous structures that coat and hold the heavy metal particles together [18,19].

3.4.1. Unconfined compressive strength (UCS) of calcined sludge blocks

The concrete blocks of the mentioned compositions were prepared and tested for UCS (Table 2). UCS of the mixtures varied with the proportions of the additives.

Fly ash upon exposure to the water of compaction, the hydrates of mixtures form cementitious pozzolanic products similar to those formed during the hydration of Portland cement. Thus, while the organic waste prevents the hardening of Portland cement, self-hardening capacity of fly ash retains higher strength than the cement accounting for higher compressive strength [20–22].

The blocks made from hydraulic molding possess higher compressive strength than the cold molding, which may be due to the avoidance of air pockets in volume matrix as a result of

the application of pressure. In both the type of molding, the cement-based system has acquired good compressive strengths than with gypsum.

3.4.2. TGA of solidified block

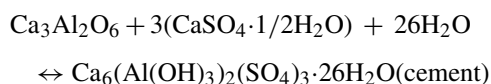
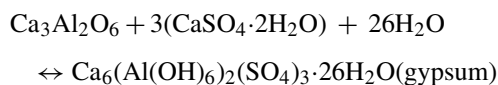
TGA of the solidified brick is presented in Fig. 8c. The weight loss of 3.65% at 91.92 °C is due to the dehydration of ettringite, which overlaps the endothermic effect of small quantities of calcium silicate hydrate. Loss of weight (2.8%) around 135.6–345.8 °C can be accounted for the deformation of the ettringite structure present in the matrix. A steep loss in the temperature range 458.91–466.76 °C clearly illustrates the elimination of calcium hydroxide and at around 700 °C there occurs an endothermic phenomenon of decarbonation due to the carbonate present in the natural pozzolan employed in the production of pozzalanic cement.

3.4.3. FT-IR of solidified block

The FT-IR spectrum of the solidified block is shown in the Fig. 9c. A broad envelope centered at 3440 cm⁻¹ can be assigned to –OH stretch of calcium hydroxide. The Si–O–Si anti symmetric stretching in hydrated cement and in fly ash is seen typically around 970 cm⁻¹. The band due to Si–O–Si symmetric stretching in the C–S–H at 943 cm⁻¹ is not clearly seen which could be due to the polymerized form of the structure. A small shoulder at 796 cm⁻¹ can be attributed to the quartz resulted from fly ash. A strong band around 1423 cm⁻¹ was assigned to calcite present in the matrix.

3.4.4. SEM-EDX Analysis

Hydration of Ca₃Al₂O₆ in the presence of cement/gypsum yields ettringite having a structure of 3CaO·Al₂O₃·3CaSO₄·nH₂O.



The ettringite phase formed favors isomorphous substitution of Al³⁺ by Cr³⁺. The SEM of cement and gypsum based system are shown in the Figs. 10 and 11.

A graphical representation of EDX showing the composition of various constituents of the solidified bricks is depicted in Fig. 12. The EDX analysis shows that the principle elements present in a micron volume region are silicon and calcium. The presence of these elements and their distribution suggest that their sources may be from calcium sulfate in cement and silica in fly ash. A minor amount of Cr³⁺ and Fe²⁺ ions is also visible. Thus, it confirms that the metals are immobilized in ettringite crystal inclusion.

3.5. Leachability studies

Leaching tests are used to assess: (a) hazardous nature of the waste, (b) effectiveness of the solid waste treatment process, and

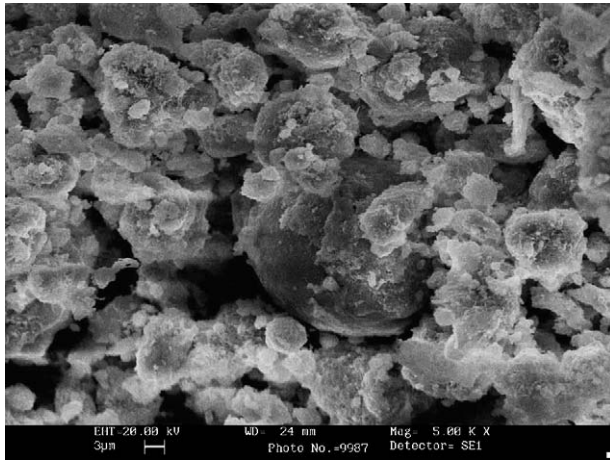


Fig. 10. SEM of the ettringite structure present in the calcined sludge (Cs); fly ash (F); cement (C) block.

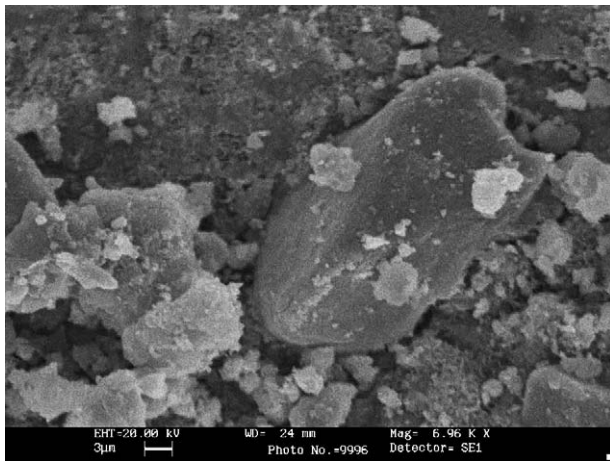


Fig. 11. SEM of the ettringite structure present in the calcined sludge (Cs); fly ash (F); gypsum (G) block.

(c) suitability of solidified and stabilized solid wastes for land co-disposal.

The concentrations of COD, Fe^{2+} and Cr^{3+} in the leachate collected at 24 h intervals for all the concrete blocks are shown in Table 3.

The moderation of pore water and high pH in the fly ash-containing concrete bricks increased the adsorption tendency of the ettringite phase, which results in the higher metal fixation

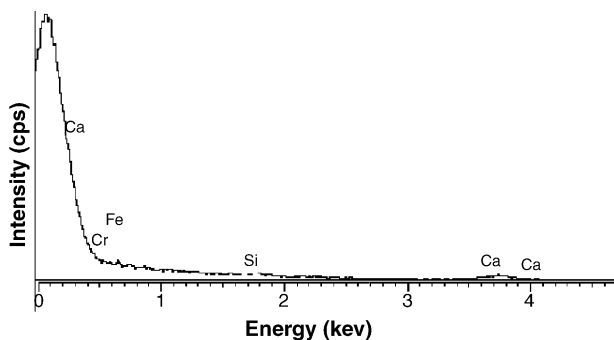


Fig. 12. EDX microanalysis of the solidified block.

Table 3

The Concentration of pollution parameters present in the leachate of cured concrete blocks

Composition of blocks	Concentration of the parameter for different hours (mg/l)					
	24	48	72	96	120	144
COD concentration (mg/l)						
Cold moulding (Cs–C–F)	60	55	47	40	37	19
Cold moulding (Cs–G–F)	50	43	39	31	17	15
Hydraulic moulding (Cs–C–F)	90	77	70	65	52	47
Hydraulic moulding (Cs–G–F)	71	64	58	50	43	30
Fe^{2+} concentration (mg/l)						
Cold moulding (Cs–C–F)	1.2	0.92	0.73	0.65	0.40	0.40
Cold moulding (Cs–G–F)	0.65	0.54	0.50	0.47	0.40	0.40
Hydraulic moulding (Cs–C–F)	3.0	2.5	1.6	1.3	0.76	0.75
Hydraulic moulding (Cs–G–F)	1.9	1.5	1.4	1.27	0.71	0.71
Cr^{3+} concentration (mg/l)						
Cold moulding (Cs–C–F)	Nil	Nil	Nil	Nil	Nil	Nil
Cold moulding (Cs–G–F)	Nil	Nil	Nil	Nil	Nil	Nil
Hydraulic moulding (Cs–C–F)	1.4	0.05	Nil	Nil	Nil	Nil
Hydraulic moulding (Cs–G–F)	1.0	Nil	Nil	Nil	Nil	Nil

property [16]. It is expected that Cr^{3+} be effectively immobilized at high pH due to the precipitation into insoluble chromium hydroxide. As the setting occurs gradually in cold moulding than in hydraulic molding better encapsulation of the metals occurred in cold moulding. 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 and 280 mg/l for Cr^{3+} and COD, respectively) [23] which proved the success of solidifying the incinerated tannery waste.

4. Conclusions

The study deals with the detailed investigation about the leaching of the tannery sludge and its breakthrough time at different conditions. Starved air combustion of tannery sludge under starved air ($\text{N}_2:\text{O}_2$ -90:10 v/v) condition at 800°C and followed by catalytic combustion over Ni coated ceramic granules at 450°C were the initial steps before solidification/stabilization which resulted in the energy recovery process. About + 1.9 kJ of energy was expended for incineration of each gram of tannery sludge in incinerator. The bottom ash was solidified/stabilized using Portland cement/gypsum and fly ash as primary binders and their unconfined compressive strength was 145 kg/cm^2 . Fly ash improved the metal fixing capacity of ettringite gel structure formed during solidification. SEM-EDX confirmed the formation of ettringite gel structure during solidification, which stabilized Cr (III) through isomorphous inclusion in the microstructure. The concentration of COD, Fe^{2+} , and 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 with out oxidizing trivalent chromium into hexavalent chromium through starved air combustion at 800°C and there is a scope for recovery of energy from sludge. The resultant bottom ash [calcined sludge (Cs)] can be solidified

and stabilized using cement/gypsum and fly ash. The solidified brick can be used as a constructional material for its compressive strength.

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