Leaching of heavy metals from hybrid bricks prepared using clay, tannery sludge, and glass powder – A comparative study of Toxicity Characteristics Leaching Procedure and Netherlands tank leaching tests

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Abstract: The work compared the leaching of heavy metals (Cr, Ni, Zn, and Pb) from the hybrid bricks using the Toxicity Characteristics Leaching Procedure (TCLP) and Netherlands tank leaching tests. Hybrid bricks were prepared by partially replacing clay with an increasing weight percentage of tannery sludge (0, 9, 18, and 27% by weight of brick specimen) and a constant weight percentage (10% by weight of brick) of glass powder. The prepared mixes were fired to 900°C, 950°C, and 1000°C to assess the leaching potential of metals from hybrid bricks at different temperatures. The TCLP test was conducted as per the United States Environmental Protection Agency (USEPA) 1311, whereas the Netherlands tank leaching test was performed as per the NEN 7345 standard. In both methods, the leaching of metals increased with the tannery sludge amounts and decreased with an increase in temperature. The release of metals from the TCLP test was slightly higher than that of the Netherlands tank leaching test. The higher amounts of metal released from the TCLP test were due to exposure to more areas of particles due to the crushing of particles. The results obtained from the TCLP test are more appropriate to the actual field conditions arising in the service life of materials.

Keywords: leaching of metals; USEPA 1311; bricks; NEN 7345

I Introduction

Animal hides undergo multiple treatments—including pretanning, tanning, and finishing—to produce commercial leather, which is widely utilized for items such as bags, belts, footwear, and wallets. The tanning process is water-intensive and employs significant quantities of salts, notably chromium salts, to cleanse and stabilize the hides. As a result, both liquid and solid wastes are generated; the solid by-product, known as tannery sludge, is often deemed hazardous due to its organic load and high chromium concentrations and is consequently sent to secured landfills [1,2]. Given the escalating volume of such sludge, there is an urgent need to explore reuse options to reduce landfill disposal. Research indicates that using industrial sludge in construction materials can mitigate disposal issues [3–16], although its organic content typically compromises material performance. Recent findings, however, show that incorporating glass powder into clay bricks enhances mechanical properties by acting as a binder when molten [17–19]. Leveraging this insight, the current study develops bricks combining tannery sludge with up to 10 wt% wet glass powder. The glass content is capped to prevent loss of cohesiveness, allowing comprehensive evaluation of the sludge's impact on brick properties. Additionally, because tannery sludge may contain heavy metals, the study assesses leaching behavior using both the TCLP and Netherlands tank leachate tests—comparing them directly to identify which method more accurately predicts contaminant mobility in these novel materials.

II Materials and methods

Materials:

The soil, tannery sludge, and glass powder utilized in this study were prepared as follows: Tannery sludge was sourced from a common effluent treatment plant in Ranipet, Tamil Nadu, India. Initially moist, it was air-dried and subsequently oven-dried at 110°C for 24 hours. Post-oven drying, the sludge formed hard lumps, which were manually disintegrated using a hammer and ground into a fine powder. This powder was stored in sealed plastic bags to prevent moisture uptake. The soil sample, obtained from a brick manufacturing facility in Kadapa, Andhra Pradesh, underwent similar treatment: it was oven-dried at 110 °C for 24 hours before being crushed to eliminate lumps. Finally, borosilicate glass collected from the Chemistry Laboratory at RGUKT RK Valley (Kadapa district, Andhra Pradesh, India) was also crushed into a fine powder. All three materials were sieved through a 150-micron standard sieve, and only the fractions passing this sieve were employed in brick fabrication.

Brick preparation:

The raw materials were combined with water to form a homogeneous slurry. Glass powder was added to constitute 10 wt % of the wet brick mixture, while tannery sludge was incorporated at levels of 9, 18, and 27 wt % of the wet mass. The wet bricks were cast with dimensions of 0.22 × 0.10 × 0.07 m and subsequently sintered in a muffle furnace at temperatures of 900 °C, 950 °C, and 1000 °C, with a heating rate of 5 °C/min. Control specimens, prepared solely from soil without any additives, were used as references.

Tests on bricks:

The leaching potential of heavy metals from tannery sludge–derived bricks was evaluated using both the Toxicity Characteristic Leaching Procedure (TCLP) and the Netherlands tank leaching test. Following the US Environmental Protection Agency’s protocol, the brick samples were first crushed and sieved to isolate particles smaller than 9.5 mm. These fine fractions were then subjected to a leaching assay employing a 0.57% (v/v) acetic acid solution. This approach ensured a rigorous assessment of heavy metal release under standardized conditions. The brick-derived solid sample was subjected to a Toxicity Characteristic Leaching Procedure (TCLP) at a solid-to-liquid ratio of 1:20. The mixture was continuously agitated at 30 ± 2 rpm for 18 hours. After this period, the leachate was separated using a 0.45 µm filter. Figure 1a and 1b shows the image of crushed particles finer than 9.5 mm and the particles agitated using jar test apparatus respectively.

a)

b)

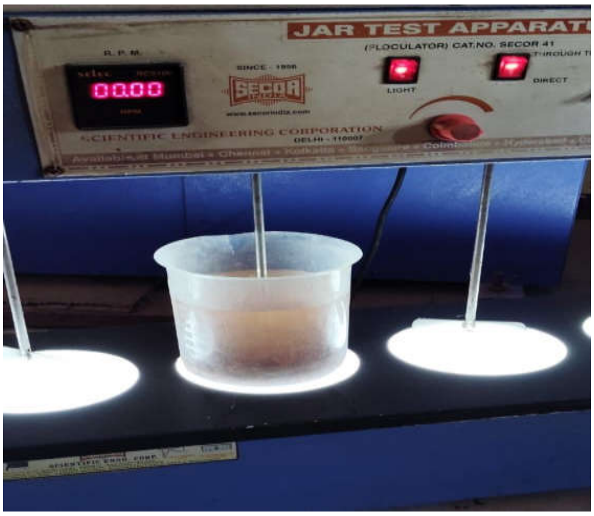

Fig 1 a) Broken brick pieces, b) particles in agitation in a jar test apparatus

The filtrate was then analyzed for heavy metal content—specifically, chromium (Cr), nickel (Ni), lead (Pb), zinc (Zn), and arsenic (As)—using inductively coupled plasma mass spectrometry (ICP-MS) [6].

The Netherlands tank leaching test, as described in NEN 7345 [21], is widely employed within the EU and the Netherlands for evaluating metal leaching from construction materials. In this procedure, a brick specimen undergoes eight sequential extractions, each with a distinct contact duration. For the initial extraction, the brick is placed in a polyethylene container filled with acidified water (pH 4), at a liquid-to-solid ratio of 5:1 by volume. The specimen is fully immersed, ensuring a minimum 5 cm clearance from the solution's surface. After 0.25 days of exposure, the brick is removed, and the leachate is filtered using 0.45-µm membrane paper before analysis by ICP-MS. The concentration of leached heavy metals from this first extraction is calculated using Equation (1).

$$E_i = \frac{(C_i - C_o)*V}{1000A} \quad \text{--------}\rightarrow (1)$$

where E_i refers to the leaching of heavy metal in the i^{th} extraction in mg/m^2, C_i is the metal's concentration in the i^{th} extraction in mg/L, C_o is the metal's concentration in the blank in mg/L, V is the solution's volume used for extraction in litres, and A is the surface area of the brick specimen in m^2. Following the initial extraction, the same brick sample was placed in a polyethylene container and replenished with a fresh leaching solution, replicating the conditions of the first extraction. It remained submerged for the second extraction, resulting in a total contact time of 24 hours. A freshly prepared leaching solution was used for successive extraction cycles on the same brick specimen. After each designated contact time, the leachate was filtered through a 0.45 µm filter paper and analyzed for heavy metal content using equation (1). Following the initial extraction, six additional sequential extractions were performed, each with a new aliquot of the leaching solution. The total contact durations for the 3rd through 8th extractions—accumulated across cycles—were 2.25 days, 4 days, 9 days, 16 days, 36 days, and 64 days, respectively [6]. Heavy metal release over the eight extractions was calculated according to equation (2).

$$E = \sum_{i=1}^{8} E_i \quad \text{-----}\rightarrow (2)$$

Figure 2 shows the specimen's submergence in the leaching solution following the NEN standards.

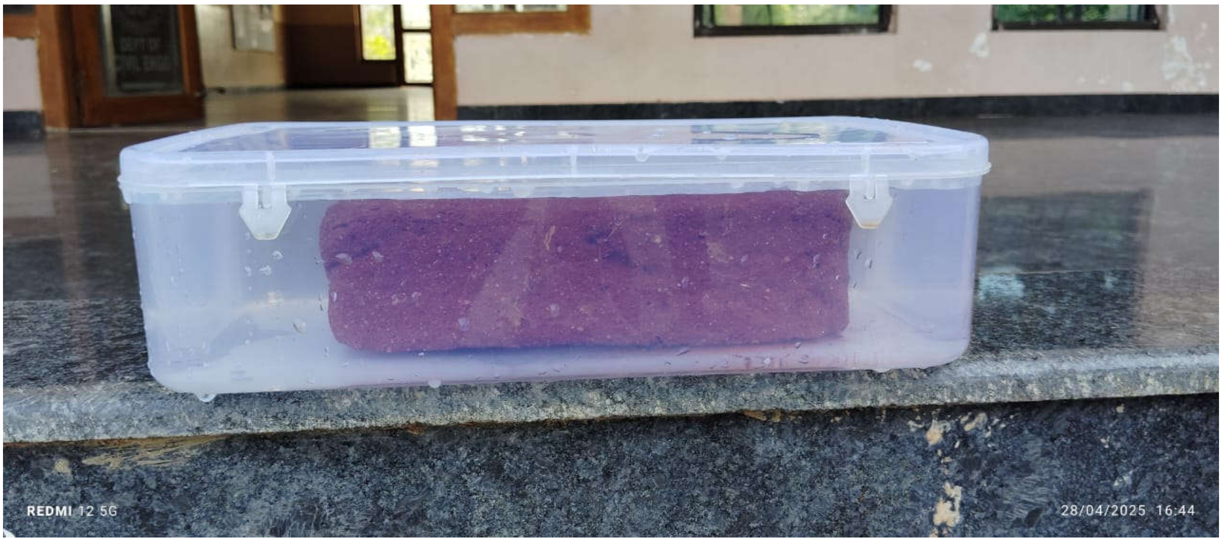

Fig. 2 Brick specimen's submergence in the leaching solution following the NEN standards

III DISCUSSION ON THE RESULTS

Heavy metal release from the bricks was evaluated against USEPA Method 1311 (TCLP) and the Dutch NEN 7345 tank leaching protocol. The results obtained from the TCLP and the NEN are given in Table 1 and 2 respectively. The USEPA permissible concentrations for Cr, Ni, Zn, and Pb are 5 mg/L, 11 mg/L, 500 mg/L, and 5 mg/L, respectively. The highest chromium leachate concentration—2.10 mg/L—occurred in bricks containing 27 wt% tannery sludge fired at 900 °C. Lead leaching peaked at 0.22 mg/L under the same conditions. Zinc remained below detection in all sludge-amended bricks. Nickel leaching reached a maximum of 0.27 mg/L in the 27 wt% sample fired to 900 °C. In both leaching protocols, increasing the tannery sludge content raised metal release, whereas higher firing temperatures suppressed it. Additionally, the crushed brick used in the TCLP test (particles <9.5 mm) exhibited greater leaching than the intact bricks tested by NEN 7345, reflecting the increased surface area exposure inherent in the TCLP method. When the material is crushed, heavy metals from its interior become exposed to the leaching solution. In the TCLP test, crushed particles are agitated in the leaching fluid for 18 hours, ensuring that all surfaces—including interior fragments—are uniformly in contact with the solution. In contrast, the Netherlands tank leaching test places uncrushed samples in leachate for a cumulative 64 days without agitation. In this setup, leaching relies on the diffusion of the solution into the brick's interior; surface metals leach quickly, but deeper metals are slower to mobilize. Moreover, the tank's container contact restricts the solution's reach on the brick's bottom surface.

Table 1 TCLP results of various heavy metals leached from TS bricks

Heavy metal	Firing temperature	0 wt% TS bricks	9 wt% TS bricks	18% TS bricks	27 wt% TS bricks	USEPA limits (mg/L)
Cr (mg/L)	1000°C	n.d	0.10	0.48	1.24	5
	950°C	n.d	0.34	0.90	1.78	
	900°C	n.d	0.54	1.35	2.10	
Ni (mg/L)	1000°C	n.d	0.05	0.11	0.20	11
	950°C	n.d	0.07	0.14	0.24	
	900°C	n.d	0.08	0.17	0.27	
Zn (mg/L)	1000°C	n.d	n.d	n.d	n.d	500
	950°C	n.d	n.d	n.d	n.d	
	900°C	n.d	n.d	n.d	n.d	
Pb (mg/L)	1000°C	n.d	0.02	0.09	0.17	5
	950°C	n.d	0.03	0.11	0.20	
	900°C	n.d	0.04	0.13	0.22	
n.d = Not detected						

Table 2 Heavy metals leached from TS bricks as per the Netherlands tank leaching test

Heavy metal	Firing temperature	0 wt% TS bricks	9 wt% TS bricks	18% TS bricks	27 wt% TS bricks	Permissible limits set by NEN 7345 [25]
Cr (mg/m^2)	1000°C	n.d	0.018	0.027	0.039	150 for U_1 and 950 for U_2
	950°C	n.d	0.058	0.077	0.095	
	900°C	n.d	0.110	0.145	0.184	
Ni (mg/m^2)	1000°C	n.d	n.d	n.d	n.d	50 for U_1 and 350 for U_2
	950°C	n.d	0.001	0.002	0.003	
	900°C	n.d	0.002	0.004	0.007	
Zn (mg/m^2)	1000°C	n.d	n.d	n.d	n.d	200 for U_1 and 1500 for U_2
	950°C	n.d	n.d	n.d	n.d	
	900°C	n.d	n.d	n.d	n.d	

Pb (mg/m^2)	1000^{o}C 950^{o}C 900^{o}C	n.d n.d n.d	0.003 0.008 0.033	0.004 0.012 0.045	0.006 0.022 0.062	100 for U_1 and 800 for U_2
n.d is not detected						
If the cumulative value of a particular heavy metal leached was less than U_1, the material can be used in constructions without restrictions. If the heavy metal leached was greater than U_2, the material is not permitted in constructions. If the results are in between U_1 and U_2 the material can be used for constructions and needs to be treated after the service life.						

As a result, TCLP typically yields higher metal release values than the Netherlands tank test. TCLP's use of crushed, agitated samples offers a more consistent assessment of total leachable metals and better simulates real-world material degradation, making its results more reliable for practical applications.

IV CONCLUSIONS

The following were the conclusions drawn from the results of the TCLP and Netherlands tank leaching tests:

1. The leaching tests revealed that metal release was markedly higher in the TCLP compared to the Netherlands tank leaching procedure. This discrepancy is largely attributed to sample crushing, which increases particle surface area and enhances exposure to the leaching medium.
2. Unlike the TCLP—where internal metal distribution within the brick has minimal impact—the Netherlands tank test is significantly influenced by metal localization inside the material.
3. Furthermore, particle size reduction plays a more critical role in metal mobilization than the duration of exposure to the leaching solution.
4. Finally, the TCLP more accurately reflects real-world field conditions encountered during the service life of construction materials.

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