INTEGRATED CHARACTERIZATION AND RECOVERY STRATEGIES FOR HOT-DIP GALVANIZING WASTES: GRANULOMETRIC, CHEMICAL, AND PHASE ANALYSIS FOR SUSTAINABLE ZINC AND IRON VALORIZATION

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Abstract

Hot-dip galvanizing (HDG) generates several zinc-and iron-bearing solid wastes—most notably top ash (zinc ash), bottom dross, galvanizing flue dust (GFD), and iron-rich sludges—whose hazardous classification is largely driven by high leachable Zn, chlorides, and associated impurities. GFD is typically an ultrafine material (particle size below 90 µm) and may contain ~27–30% Zn and significant chloride/ammonium phases, making targeted hydrometallurgical recycling attractive at small scale.

This paper synthesizes an "integrated characterization-to-flowsheet" strategy for HDG wastes, combining granulometric and morphological diagnosis, bulk chemical/impurity constraints, phase assemblage (chlorides/oxides/hydroxychlorides/intermetallics), and (iv) recovery route selection (selective leaching–purification–electrowinning; oxide/pigment valorization; immobilization where recycling is not feasible). From the analyzed literature set, robust recovery is demonstrated for GFD via two-step leaching and zinc production, GFD residue via concentrated acid leaching achieving very high Zn concentration and efficiency (e.g., 136.532 g/L and 96.24% Zn leached at 4 M H_2SO_4, L/S = 3, 10 min), (c) top ash via sulfuric leaching and electrowinning under controlled pH/current density, and (d) iron sludge valorization to hematite pigments after calcination/washing with major Zn/Cl removal.

A decision matrix is proposed linking waste "fingerprints" to optimal zinc/iron valorization pathways, including emerging conversion of zinc-bearing solutions into ZnO ceramic nanofibers by electrostatic spinning.

Keywords

hot-dip galvanizing; galvanizing flue dust; top ash; sludge; granulometry; XRD; leaching; electrowinning; zinc recovery; iron pigments

1. INTRODUCTION

Zinc-based coatings remain a dominant corrosion-protection technology for steel, and HDG is widely applied across batch and continuous lines. In the HDG process, steel parts are immersed in molten zinc at about 450–470 °C, following pre-treatment steps (degreasing, pickling, fluxing) that strongly influence the chemistry of generated wastes [2]. Solid wastes include top ash, bottom dross, and galvanizing flue dust (GFD), while additional iron-rich sludges are produced from related chemical operations [2].

Among these streams, GFD is particularly challenging: it forms as "white fumes" above the zinc bath due to decomposition of flux constituents and reactive chloride chemistry, producing very fine particles, "in fumes, a large fraction under 1 µm" that are captured on filtration systems [2]. The waste is commonly classified as hazardous (due to high leachable Zn/chlorides and associated metals), yet it is also a valuable secondary zinc source [1].

The literature indicates that "one-size-fits-all" recycling does not exist across HDG wastes: top ash can be rich in metallic Zn/oxides/hydroxychlorides, GFD is dominated by zinc ammonium chloride and ultrafine particle size, and sludges can be iron-rich with problematic Zn/Cl contaminants [1,3,6]. Therefore, integrated characterization (granulometry + chemistry + phases) is not "extra"—it determines the feasible recovery route, impurity management, and final product portfolio (Zn metal/ZnO/flux reuse/Fe pigments/immobilized residues).

This paper proposes and justifies an integrated characterization-to-recovery framework for HDG wastes, synthesizing (i) key diagnostic measurements and (ii) compatible flowsheets for zinc and iron valorization, using only the selected eight studies [1,4,5].

2. Materials and Methods (Literature-Derived Framework)

This study is a structured synthesis of eight peer-reviewed sources focused on HDG waste characterization and/or recovery processing [1–8]. "The following sections define..." below define a reproducible framework that converts reported measurements into a unified flowsheet selection logic.

2.1. Waste stream classification and sampling logic

The HDG solid wastes considered are:

- Galvanizing flue dust (GFD): ultrafine particulate captured from white fumes above the bath; particle size below 90 μm in characterized samples [1].
- GFD residue: undissolved solid remaining after an initial "environmentally friendly" hydrometallurgical processing step; contains high Zn in oxide/chloride form [2].
- Top ash (zinc ash): formed on bath surface: reported as containing 63% Zn as metallic, oxide and hydroxychloride phases [3].
- Iron-rich sludges / $ZnCl_2$ production sludges: iron oxide–bearing materials with Zn/Cl impurities; can be upgraded to hematite pigment after washing/calcination [6].
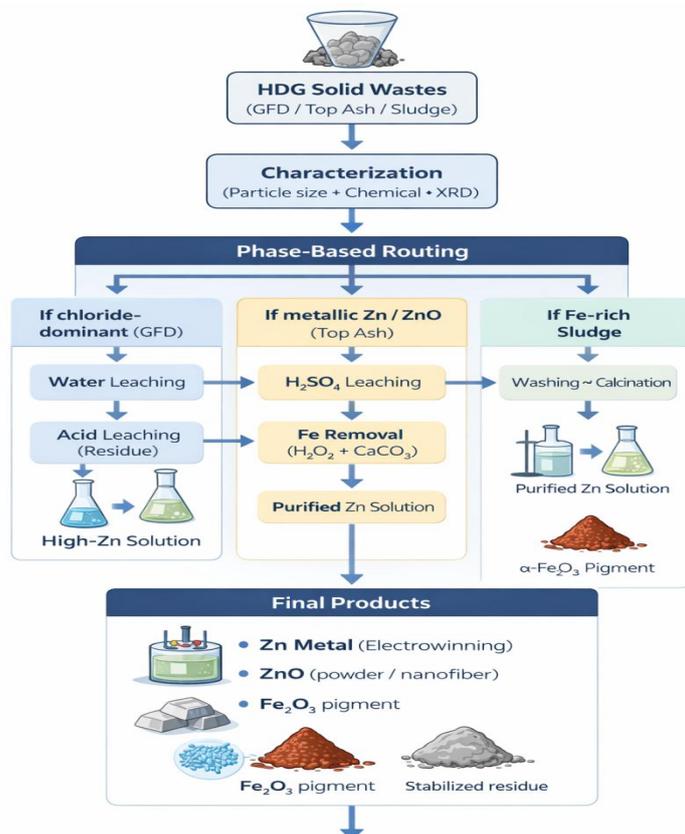
Fig. 1. *Integrated characterization-to-recovery framework for hot-dip galvanizing wastes, illustrating the sequential role of granulometric analysis, chemical composition, and phase identification (XRD/SEM-EDS) in selecting suitable zinc and iron valorization routes.*

2.2. Granulometric and morphological diagnostics

Granulometry is used to predict:

- leaching kinetics (fine particles → fast dissolution),
- filtration behavior (ultrafines → poor filterability),
- dust hazard and handling constraints,
- required pre-treatment (agglomeration/washing).

2.3. Chemical composition and impurity constraints

Bulk chemistry (e.g., AAS/XRF/ICP) is used to:

- quantify Zn and Fe resources,
- identify impurities that impact product purity and electrochemistry (Al, Pb, etc.),
- estimate potential value vs disposal cost.

Example reported GFD chemistry includes Zn 27.46% and impurities such as Al (0.38–1.03%), Fe (0.33%), Pb (0.07%) [1].

2.4. Phase analysis: identifying "why" zinc is (or isn't) easily recovered

XRD + SEM-EDS are used to differentiate:

- water-leachable ammonium–zinc chlorides vs
- non-water-leachable ZnO/other oxides,

which directly supports selective, staged leaching.

For GFD, reported dominant phases include $(NH_4)_2ZnCl_2$ and $(NH_4)_2ZnCl_4$, and the recommended hydrometallurgical strategy is explicitly two-step: water leaching followed by acid leaching for the remaining Zn-bearing solid phases [1].

2.5. Synthesis of process routes and performance evaluation

Processing performance is synthesized from reported leaching/electrowinning outcomes:

- GFD residue leaching: optimal reported case: L/S = 3, 4 M H_2SO_4, ambient temperature, 10 min → Zn = 136.532 g/L, Zn leaching efficiency = 96.24% (low Fe co-dissolution) [2].
- Top ash recovery: leaching in 20% H_2SO_4 at 100–150 g/L ash; iron removal using H_2O_2 + $CaCO_3$; electrowinning at pH 0.1–1.0 and 3–6 A/dm² for pure zinc [3].
- Sludge-to-pigment upgrading: washing/calcination strategies can reduce Zn and Cl up to 97% and increase Fe_2O_3 from ~41% to ~98% with hematite formation (α-Fe_2O_3) [6].
- Emerging valorization: ZnO ceramic nanofibers from GFD-derived solutions by electrospinning; 0.5 M HCl gives oval fibers, 0.5 M H_2SO_4 gives hollow ribbon morphology [8].

3. Results and Discussion

3.1. "Fingerprinting" HDG wastes: what granulometry + phases reveal

3.1.1. Galvanizing flue dust (GFD): ultrafine, chloride-dominated, hazardous—but highly recoverable

GFD formation is chemically linked to flux decomposition and chloride reactions; the resulting waste is fine-grained, hazardous, and rich in leachable Zn/chlorides [2].

The characterized GFD samples show a particle size below 90 μm and are dominated by ammonium–zinc chlorides, specifically $(NH_4)_2ZnCl_2$ and $(NH_4)_2ZnCl_4$ [1].

This phase assemblage explains the strong case for selective staged leaching:

- Water leaching targets readily soluble chloride salts, achieving around "approximately 60%" Zn recovery in the first step in reported tests, while keeping Fe very low [1].
- Acid leaching then recovers the remaining Zn from non-water-leachable phases (e.g., ZnO and related solids) [1].

From a product perspective, the proposed hydrometallurgical approach enables high-purity zinc (metal or oxide) at small scale, which is important because GFD generation quantities can be relatively low (reported around 0.3 kg per tonne of galvanized steel in one study), making large centralized pyrometallurgy less attractive [1].

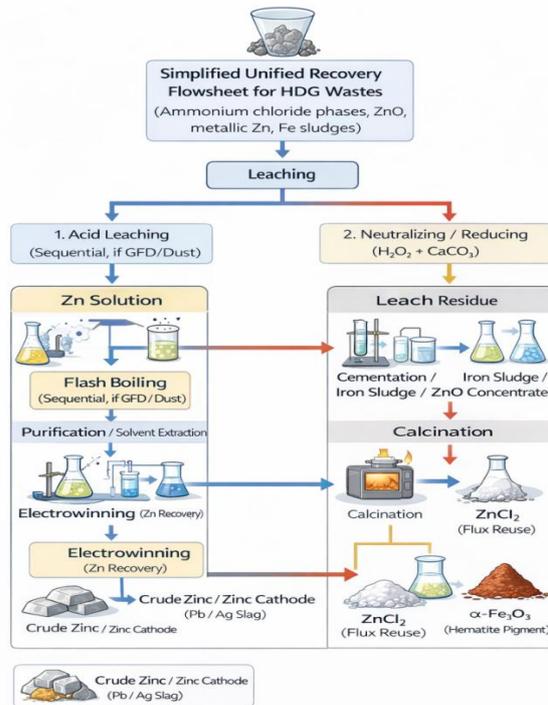**Two-step GFD leaching logic: water-soluble chloride phase removal → acid dissolution of ZnO-rich residue**

Fig. 4. *Schematic illustration of the two-step hydrometallurgical leaching strategy for galvanizing flue dust (GFD): (i) initial water leaching to dissolve ammonium–zinc chloride phases, followed by (ii) acid leaching of the ZnO-rich solid residue to achieve high overall zinc recovery.*

3.1.2. GFD residue: "secondary resource" with high Zn loading

A crucial practical issue is that "environmentally friendly" initial processing may leave a Zn-rich residue. The reported residue contains 42.46% Zn and includes oxygen and chlorine signals consistent with oxides/chlorides [2].

This residue is therefore not a "waste of a waste" but a concentrated zinc resource.

The literature provides a strong performance benchmark: leaching at L/S = 3 with 4 M H_2SO_4 at ambient temperature for 10 minutes produced Zn = 136.532 g/L with 96.24% leaching efficiency, while Fe remained low (0.233 g/L; 5.97% leached) [2].

This is significant because high Zn concentration is directly beneficial for downstream electrowinning economics and equipment sizing, provided chloride management and impurity control are adequate.

3.2. Top ash (zinc ash): balancing zinc recovery with iron control

Top ash is chemically different from GFD. It is reported to contain 63% Zn distributed across metallic, oxide, and hydroxychloride phases [3].

This mixture creates two competing needs:

1. Dissolve Zn efficiently (including metallic Zn/oxides), and
2. Prevent iron from contaminating the electrolyte and harming zinc cathode quality.

The selected study provides a full hydrometallurgical "loop-to-bath" strategy: leach top ash in 20% H_2SO_4 at 100–150 g/L loading; remove iron by $Fe_2O_3 \cdot xH_2O$ precipitation using H_2O_2 and $CaCO_3$; and electrowin zinc at pH 0.1–1.0 under yielding pure metal [3].

The important insight is that purification is not optional; the iron pathway and electrolyte pH window govern zinc deposit purity and operational stability.

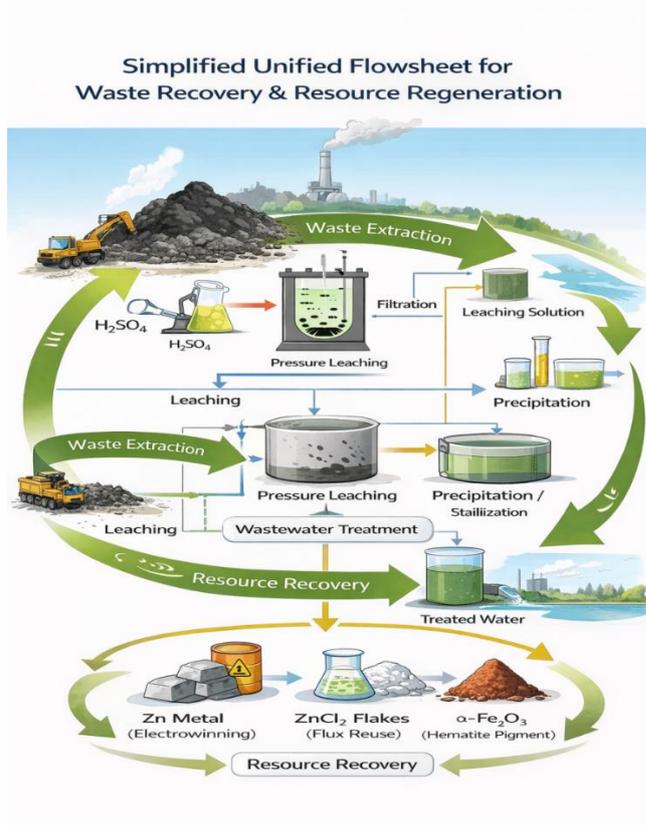**Top ash recycling route: H_2SO_4 leach → Fe removal → Zn electrowinning**

Fig. 5. *Simplified recycling route for hot-dip galvanizing top ash, consisting of sulfuric acid leaching (H_2SO_4), iron removal by oxidative precipitation using H_2O_2 and $CaCO_3$, followed by zinc electrowinning under controlled pH conditions.*

3.3. Iron-rich sludges: shifting from "metal recovery" to "product upgrading"

Not all HDG-associated wastes should be treated solely as zinc resources. Some sludges are better approached as iron product precursors with Zn/Cl as impurities to be removed. The pigment-focused study demonstrates that thermal treatment can dramatically reduce Zn and Cl (up to 97% reduction) and increase Fe_2O_3 content from ~41% to ~98%, with XRD confirming α-Fe_2O_3 (hematite) [1].

This converts a problematic sludge into a functional pigment usable in glazes, creating a higher-value outlet and reducing landfill reliance.

This "upgrade" logic is a critical component of an integrated strategy: when zinc is chemically/operationally expensive to recover from an iron-rich sludge, removing Zn/Cl and valorizing iron as hematite can be the more sustainable route.

3.4. Emerging valorization: ZnO ceramic nanofibers from GFD-derived solutions

Beyond conventional zinc metal/ZnO powders, one study demonstrates conversion of GFD-derived zinc solutions into ZnO ceramic nanofibers via electrospinning—an example of "advanced materials" valorization. Both acids (HCl and H_2SO_4) were suitable; 0.5 M HCl produced oval fibers, while 0.5 M H_2SO_4 produced hollow ribbon morphologies, potentially associated with higher surface area [8].

This provides an additional innovation path where market context and product certification can justify more complex processing.

3.5. Integrated decision matrix: choosing the right route for each HDG waste

Based on the reported evidence, route selection can be formalized as a decision matrix using:

- Granulometry (ultrafine vs coarse; filtration risk),
- Dominant phases (ammonium–zinc chlorides vs ZnO vs metallic Zn),
- Impurities (Al/Pb/Fe behavior),
- Chloride management burden, and
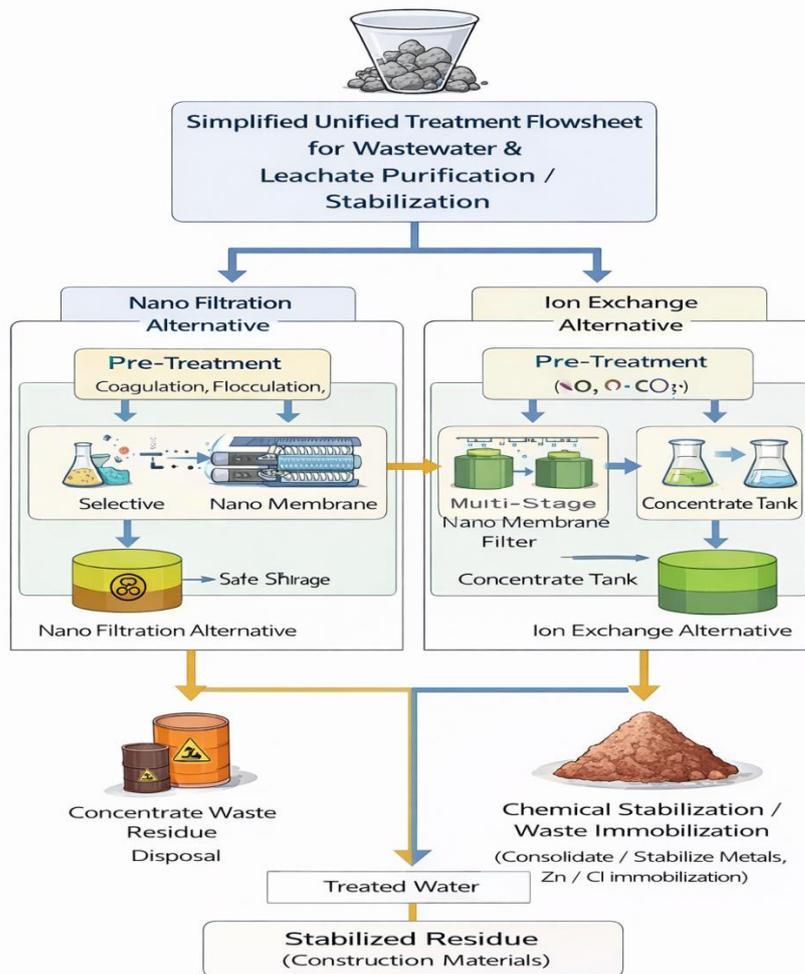 - Target product (Zn metal, ZnO, flux reuse, Fe pigment, immobilized residue).

Fig. 7. *Simplified decision matrix (flowchart) linking key characterization outputs—particle size distribution and phase composition—to appropriate recovery, valorization, or immobilization pathways for hot-dip galvanizing wastes.*

4. Conclusions

1. Integrated characterization is the "gatekeeper" for HDG waste recovery. Granulometry and phase assemblage directly determine whether staged leaching, direct acid leaching, or product upgrading is most appropriate. GFD is ultrafine and chloride-dominated, with main phases $(NH_4)_2ZnCl_2$ and $(NH_4)_2ZnCl_4$, justifying two-step leaching (water $\rightarrow$ acid)

2. GFD residue is a high-grade zinc secondary resource. Reported processing achieved Zn = 136.532 g/L and 96.24% Zn leaching at 4 M H_2SO_4, L/S = 3, 10 min, while keeping Fe relatively low, supporting practical downstream zinc recovery.

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3. Top ash recycling requires strict iron control. A complete route (20% H_2SO_4 leach $\rightarrow$ Fe precipitation using $H_2O_2/CaCO_3$ $\rightarrow$ electrowinning at pH 0.1–1.0 and 3–6 A/dm^2) demonstrates that electrolyte chemistry governs product purity and operability.

4. Iron-rich sludges can be best valorized as iron products. Calcination/washing can remove Zn/Cl up to 97% and upgrade to ~98% Fe_2O_3 with hematite formation, enabling pigment/glaze use and diversifying the product portfolio beyond zinc metal.

5. Advanced-material valorization is feasible (ZnO nanofibers) and may be attractive where markets support higher-value products; acid choice influences nanofiber morphology (0.5 M HCl oval fibers vs 0.5 M H_2SO_4 hollow ribbons).

5. References

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