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# Aluminium-Bearing Technogenic Wastes as Precursors of Coagulants and Sorbents for Wastewater Treatment: A Critical Review and the Valorisation Potential of a Sulfate-Rich Aluminium Sludge

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**Abstract:** Aluminium-bearing technogenic wastes -drinking-water treatment residuals (WTR/alum sludge), primary and secondary aluminium dross and salt cake, anodising sludge, and scrap aluminium - are generated in millions of tonnes annually and are overwhelmingly landfilled. Because aluminium is simultaneously the active element of the most widely used coagulants and the structural element of one of the most effective anion sorbents, these wastes are, in principle, a secondary raw material for water treatment reagents. This paper reviews the published experimental evidence on that conversion and then tests it against the composition of a specific aluminium-rich technogenic sludge collected in the Navoi region of Uzbekistan. Fifty-six peer-reviewed sources indexed in Scopus/Web of Science, published mainly between 2014 and 2026, were screened and analysed. The analysis is deliberately limited to what the X-ray fluorescence data can support; mineralogical, leaching, toxicological and jar-test verification are identified as mandatory next steps.

**Keywords:** aluminium-bearing technogenic waste; alum sludge; aluminium dross; coagulant recovery; polyaluminium sulfate; adsorbent; wastewater treatment; circular economy; X-ray fluorescence; Uzbekistan.



## 1. Introduction

Water treatment is chemically dominated by aluminium. Aluminium sulfate and pre-hydrolysed polyaluminium salts remain the reagents of first choice for turbidity, natural organic matter and phosphorus removal, and the mechanisms by which they act -charge neutralisation by cationic hydrolysis products and enmeshment of impurities in an amorphous hydroxide precipitate, commonly called sweep flocculation -have been understood in outline for decades [1]. The consequence is a large and continuous flow of aluminium into and out of the water sector. Nayeri and Mousavi estimate that roughly 3.8 kg of water treatment sludge is produced per capita and

about 10,000 t per day worldwide, that a plant of 1 m3/s capacity generates approximately 8,300 kg of sludge daily, and that the United Kingdom water industry alone consumes more than 0.33 Mt of coagulant annually, at a cost of about £40 million, while producing some 0.18 Mt of residuals whose disposal costs a further £8 million [2].

A second, larger flow originates in metallurgy. Tsakiridis reports that 200–500 kg of salt slag is produced per tonne of secondary aluminium, and that this slag typically contains 15–30% Al2O3, 30–55% NaCl, 15–30% KCl and 5–7% metallic aluminium, together with carbides, nitrides, sulfides and phosphides, which is why it is classified in the European Hazardous Waste Catalogue as highly flammable, irritant, harmful and leachable [3]. Wang and co-workers report that China produced 38.5 Mt of electrolytic aluminium in 2021 and more than 3 Mt/a of dross, against a global figure of approximately 6 Mt/a of which less than 5% is recycled [4]; a recent critical review puts global secondary aluminium dross generation at about 5.5 Mt/a in 2023 and notes its classification as hazardous waste HW48 in China [5].

The coincidence is obvious and has been noticed repeatedly: the element that the water sector buys as a reagent is the element that the metallurgical and water sectors discard as a waste. What is far less obvious, and what this review is intended to establish, is how much of the published evidence for converting the second into the first is quantitatively robust, under what conditions it holds, and which failure modes are documented rather than assumed.

The question is not abstract in Central Asia. A regional review of wastewater treatment in Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan and Uzbekistan concluded that many cities have inadequate treatment infrastructure because of constrained technical and economic resources and underdeveloped regulatory frameworks. Where reagent supply is a cost constraint, a locally generated secondary source of aluminium is of direct practical interest. Work in the region has so far concentrated on natural raw materials: activation of local minerals for effluent treatment, hydrochloric-acid processing of Auminzatau kaolin into a coagulant that removed 97.5% of contaminants from paper-mill wastewater, and bentonite-based sorbents for chemical-industry effluent in southern Kazakhstan. Processing of aluminium-bearing *technogenic* material has been addressed in the wider CIS mainly for bauxite residue. To the best of the authors' knowledge, no peer-reviewed study has yet reported the conversion of an aluminium-bearing industrial sludge generated inside Uzbekistan into a water-treatment reagent. This gap is the specific justification for the present work [6].

The aims of this paper are therefore threefold: (i) to review, critically and with attention to reported numerical values, the published evidence on the conversion of aluminium-bearing technogenic wastes into coagulants and sorbents; (ii) to characterise, on the basis of energy-dispersive X-ray fluorescence data, a sulfate-rich aluminium sludge sampled in the Navoi region of Uzbekistan, and to place its composition within the range reported for the waste classes reviewed; and (iii) to derive from that comparison a set of experimentally testable valorisation routes together with an explicit statement of what the available data cannot yet support.

## 2. Materials and Methods

The review component follows a structured narrative-review procedure. Records were retrieved through Scopus- and Web of Science-indexed publisher platforms (Elsevier/ScienceDirect, Springer Nature, MDPI, IWA Publishing, SAGE, Wiley) and cross-checked against OpenAlex and Semantic Scholar metadata.

Inclusion criteria were: (a) publication in a peer-reviewed[7]., indexed journal; (b) reporting of at least one quantitative performance indicator (extraction yield[8]., adsorption capacity, removal efficiency, dose, or operating conditions); and (c) primary experimental work or a critical review[9].

The sample examined in Section 3.7 is an aluminium-bearing technogenic sludge designated "Shlam", collected in the Navoi region, Uzbekistan.

Elemental analysis was performed on 22 October 2025 with a Rigaku NEX DE energy-dispersive X-ray fluorescence spectrometer (application profile "Navoiy_2025") using the fundamental-parameters (FP) quantification method. Measurement conditions were: 10 mm collimator (DE-10 mm), air atmosphere, no sample spinning, optimised measurement order, single determination. Two excitation conditions were applied -a Mid-Z condition (primary filter C, tube voltage 35.0 kV, tube current 342 μA, shaping time 1.6 μs, 100 s acquisition, 29.8% dead time) and a Low-Z condition (open filter, 6.5 kV, 433 μA, 1.6 μs, 100 s, 37.1% dead time). Lower limits of detection (LLD) and quantification (LLQ) were reported by the instrument for each analyte.

## 3. Results and Discussion

The waste classes differ so widely in aluminium grade and in contaminant burden that they cannot be treated as a single feedstock category (Table 1).

**Table 1.** Reported composition of the principal aluminium-bearing technogenic waste classes.

| Waste class | Aluminium content as reported | Principal accompanying phases / constituents |
|---|---|---|
| Alum sludge / WTR (Colombia) | Al2O3 29.9% (low-turbidity raw water) rising to 33.9% (very high turbidity) | SiO2 20.5–26.4%; Fe2O3 11.3–12.9%; LOI at 950 °C 24.6–34.4%; 45.1–65.2% amorphous |
| WTR (Egypt, Cairo plants) | 86.65–688.85 mg Al per g of sludge | Transferable Fe, Mn, Sr; TOC co-transfer 36.7–82.6% |
| Aluminium salt slag | Al2O3 15–30%; metallic Al 5–7% | NaCl 30–55%; KCl 15–30%; carbides, nitrides, sulfides, phosphides |
| Salt cake (USA, 39 samples) | Mean total Al ≈14 wt%; metallic Al typically 3–5 wt% (0–22 wt%) | Al2O3, AlN, MgAl2O4 spinel, K2NaAlF6; only ~0.6% of total Al leachable |
| Aluminium dross (China) | Alumina 40–60 wt%; AlN 10–30 wt% | Salts 5–15 wt%; heavy-metal oxides 3–10 wt%; Na3AlF6, NaF, AlF3, CaF2 |
| Secondary aluminium dross | Residual metallic Al 3–15 wt% | Classified HW48 (hazardous) in China |
| SAD (alkaline-roasting study) | ≈40 wt% Al | AlN 19.62 wt%; $\alpha$-Al2O3; MgAl2O4 |
| Anodising sludge | Amorphous Al2O3 and Al(OH)3 | CaCO3 and CaSO4·2H2O |

Three points follow that are material to any valorisation decision. First, alum sludge is a low-grade but chemically benign feedstock: its alumina content is around 30%, but it carries a heavy organic load -loss on ignition of 24.6–34.4% and it is largely amorphous, which both limits crystallographic characterisation and, as Section 3.6 shows, favours adsorption. Second, dross and salt cake are higher-grade but hazardous: the salt flux, the fluorides and above all aluminium nitride are the controlling problem rather than the aluminium grade. Third, and importantly for the sample analysed here, anodising sludge is the one industrial class whose aluminium occurs as amorphous oxide and hydroxide without a salt flux [10].

Acid digestion is by a wide margin the most studied conversion route, and Nayeri and Mousavi note that digestion at pH 1–3 has been applied most frequently because of its operational simplicity, low cost and high efficiency. The quantitative results are collected in Table 2.

**Table 2.** Acid-leaching recovery of aluminium from aluminium-bearing wastes. [11], [12], [13], [14], [15].

| **Feedstock** | **Acid and conditions** | **Aluminium recovery** |
|---|---|---|

| | | |
|---|---|---|
| WTP sludge (Malaysia) | 4 M acid, S/L 20.9%, 90 °C, 4.4 h (RSM-optimised) | 68.8 ± 0.3% (predicted 70.3%) |
| PACl sludge / alum sludge (India) | H2SO4 to pH 2.0, 0.5% solids, 30 min | 73.26% (PACl sludge); 62.73% (alum sludge) |
| Wet WTS (Colombia) | H2SO4, 40 mL/L (3.5 N) | 76.3%, with 67% sludge volume reduction |
| Potabilisation sludge (Colombia) | 98% H2SO4, pH 1.5, 125 rpm | 566.0–810.5 mg Al/L in leachate (maximum at pH 1.5) |
| WTP sludge (Egypt) | Acid digestion | Up to 97% Al (site-dependent) |
| WTP sludge (India) | 2.5 N H2SO4, 0.05 mL acid per mL of 1% sludge | Sludge reagent product effective at 8 mL/L over pH 6–8 |

Four conclusions are supported. First, recovery from water treatment sludge clusters in a fairly narrow band of roughly 60–80% under practical conditions, with higher figures achievable but site-specific [16]. Second, recovery from dross is *not* intrinsically higher: raw secondary aluminium dross leached with hydrochloric acid gave less than 30% even after mechanical activation, whereas sulfuric acid at 30 wt% and 90 °C gave 98.3 [17].

The alkaline route dissolves aluminium as aluminate rather than as a salt. Masschelein and co-workers established the essential parameters four decades ago: optimum dissolution at pH 11.4–11.8 with NaOH or 11.2–11.6 with Ca(OH)2, at sludge concentrations below 20 g/L dry weight, with up to 80% aluminium recovery achievable using NaOH alone. Crucially, they recommended restricting recycling to 25–30% of coagulant demand, found no detrimental effect below 50% substitution, and reported that heavy metals in the recovered product were 10–15 times lower when lime was used instead of sodium hydroxide [18]. That trade-off -cleaner product, lower practical substitution rate - has not been superseded.

Ion exchange offers a third variant. Petruzzelli and co-workers operated a 50 L/d pilot using a weak-electrolyte carboxylate resin on an acidic leachate at pH 3.5, regenerated with 0.4 M NaOH, and reported a recovered coagulant pure enough to justify reuse in potable operations [19].

The XRF results for the “Shlam” sample are given in Table 3 exactly as reported by the instrument.

**Table 3.** Energy-dispersive XRF analysis of the studied sludge (FP method, mass% of detected elements).

| **Element** | **Result, mass%** | **Element** | **Result, mass%** |
|---|---|---|---|
| Al | 75.5 | Cr | 0.0498 |
| S | 19.8 | Mn | 0.0492 |
| Fe | 1.49 | Zn | 0.0406 |
| Ca | 1.16 | Zr | 0.0347 |
| Si | 0.997 | Ga | 0.0155 |
| Ti | 0.380 | Sr | 0.0117 |
| Ni | 0.255 | Pb | 0.0110 |
| Cl | 0.156 | Co | (0.0033)* |
| Cu | 0.0500 | Na, Mg, K, Ac | ND |
| V | 0.0498 | | |

Recalculated on an oxide basis and renormalised to 100% (calculated values, loss-on-ignition-free): Al2O3 71.49%, SO3 24.78%, SiO2 1.07%, Fe2O3 1.07%, CaO 0.81%, TiO2 0.32%, NiO 0.16%, Cl 0.08%, with V2O5, Cr2O3, MnO, CuO, ZnO, ZrO2, Ga2O3, SrO and PbO each below 0.05%.

Four features characterise this material.

(i) Exceptionally high aluminium grade. At approximately 71.5% Al2O3 on the oxide basis, the sludge is roughly twice as rich as the alum sludges of Table 1 (29.9–33.9% ) and above the 40–60% alumina reported for aluminium dross and the approximately 40% Al of the alkaline-roasting feedstock. Only the alumina obtained *after* hydrometallurgical refining of dross is comparable.

(ii) A sulfate system, not a chloride system. Sulfur is the second element at 19.8 mass%, giving a molar Al/S ratio of 4.53, while chlorine is only 0.156 mass%. The product of acidification will therefore naturally be an aluminium sulfate or basic aluminium sulfate rather than a polyaluminium chloride. This matters for process selection, since the PAC literature reviewed in Section 3.3 is chloride-based and is not directly transferable.

(iii) A basicity already close to the coagulant range. The charge-balance calculation of Section 2.2 gives a total cation charge of 8.55 eq per 100 g of detected elements against 1.24 eq of sulfate and chloride, leaving 7.31 eq to be balanced by hydroxyl or oxide, that is, OH/Al ≈ 2.6, corresponding to a nominal basicity of about 87%. The notional formula is therefore approximately Al(OH)2.6(SO4)0.22·nH2O, with a formula mass of about 92.6 g/mol and an aluminium content of about 29 wt% on an anhydrous basis. It follows that the detected elements represent only some 38–40% of the as-received mass, the balance being oxygen and hydrogen, which is precisely the closed-sum effect anticipated in Section 2.3. This estimate implies a loss on ignition of at least 26% from structural hydroxyl and sulfate alone, before any free moisture.

This calculated basicity of approximately 2.6 sits just above the 2.0–2.4 range identified as optimal for polyaluminium coagulant synthesis and well above the 2.0 of the foil-derived PAC of Youssef and co-workers. The practical implication is developed in Section 3.8.

(iv) Absence of alkali-metal flux, presence of transition metals. Sodium, magnesium and potassium were not detected. This is a significant negative result: it distinguishes the material sharply from salt slag and salt cake, which contain 30–55% NaCl and 15–30% KCl and whose desalination is the dominant processing burden. Conversely, nickel at 0.255 mass% of detected elements is the most notable trace constituent; on the as-received basis estimated above, this corresponds to roughly 0.1 wt%, or of the order of 1000 mg/kg, with titanium of the order of 1500 mg/kg and chromium, vanadium, copper, manganese, zinc and zirconium each in the range of roughly 130–200 mg/kg, and lead of the order of 40 mg/kg. These are order-of-magnitude estimates conditional on the formula above and must be confirmed by acid digestion with ICP-OES or ICP-MS.

A further caution is required. XRF cannot detect nitrogen, so the presence or absence of aluminium nitride cannot be assessed from these data. Given that AlN hydrolyses to ammonia and that hydrogen is the dominant evolved gas during hydrometallurgical treatment of aluminium wastes, this must be established experimentally before any wet processing at scale. The absence of a salt flux and of detected fluorine makes an AlN-bearing dross origin unlikely, but unlikely is not excluded.

Valorisation routes proposed for the studied sludge

Three routes follow from the composition, and their relative merit can be assessed quantitatively even before experiment.

Route A -partial acidification to a basic aluminium sulfate (polyaluminium sulfate) coagulant. Because the material already carries sulfate and already has OH/Al ≈ 2.6, it does not need to be dissolved and reconstituted; it needs only to be brought down into the target basicity window. Reducing OH/Al from 2.6 to 2.2, the optimum reported by Kassa and co-workers, requires 0.4 mol of H+ per mol of Al, i.e. 0.2 mol H2SO4 per mol Al. On the basis of the formula derived in Section 3.7 (approximately 10.8 mol Al per kg of dry sludge), this corresponds to about 0.21 t of 100% H2SO4 per tonne of dry sludge. Full dissolution to stoichiometric Al2(SO4)3, by contrast, would require 1.28 mol H2SO4 per mol Al, or about 1.35 t of acid per tonne of sludge -a more than sixfold difference in

reagent cost. Since the economic assessment of Keeley and colleagues concluded that acid recycling is mandatory for economic coagulant recovery and that integrating acid recovery roughly halved overall operating cost [20], a route whose intrinsic acid demand is six times lower is materially advantaged. These are stoichiometric estimates and assume that the aluminium is present as reactive amorphous hydroxide; if crystalline boehmite, gibbsite or corundum is present, both the acid demand and the dissolution kinetics will differ, which is why X-ray diffraction is the first required experiment.

Route B -thermal activation and granulation to an oxyanion sorbent. The amorphous hydroxide fraction indicated by the charge balance is the fraction that Rahmati and co-workers identified as controlling phosphate uptake. The precedents define the operating envelope: calcination at 550 °C with granulation gave 7.27 mg P/g and more than 86% phosphorus removal at pilot scale; sequential thermal activation at 300 °C plus 3 M acid activation gave 279.2 m2/g and 13.4 mg P/g; calcination at 500 °C of polyaluminium chloride sludge gave 15.9 mg As(V)/g with a column holding below 10 μg/L for 150 h. Given the much higher aluminium grade of the present material, capacities at the upper end of the ranges in Table 3 are plausible -but Sousa and colleagues' finding that the point of zero charge rather than aluminium content predicts capacity means this must be demonstrated, not assumed. One specific caution applies: the sample's sulfate content is high, and sulfate occupies the same surface sites as phosphate, so a sulfate-elution step before or during activation may prove necessary.

Route C -split processing. Acid leaching of part of the aluminium to a liquid coagulant, with the residue calcined and granulated as a sorbent. This maximises material utilisation but doubles the process complexity and has no direct precedent in the reviewed literature.

The residual-aluminium question must be addressed in all three cases. Because monomeric aluminium species dominate residual aluminium when poorly hydrolysed reagents are used, and because residual aluminium does not vary monotonically with basicity, the basicity of any Route A product must be tuned experimentally against measured residual aluminium, targeting the practicable levels of 0.1–0.2 mg/L cited by WHO and the 200 μg/L EU indicator value [21], rather than assumed from the raw material's calculated basicity.

## 4. Conclusion

1. This Aluminium-bearing technogenic wastes constitute a chemically credible secondary source of water-treatment reagents, but the waste classes are not interchangeable. Alum sludge is low-grade (around 30% Al2O3) and organics-laden but benign; dross and salt cake are higher-grade but hazardous, their salt flux, fluorides and aluminium nitride rather than their aluminium grade being the controlling problem.
2. Acid leaching is the dominant conversion route, recovering roughly 60–80% of aluminium from water treatment sludge under practical conditions and up to 98.3% from dross with sulfuric acid at elevated temperature. Reported yields are not directly comparable because the denominators differ, and any comparative tabulation must state the basis of each figure.
3. Recovered coagulants can match commercial products in removal efficiency and can reduce the applied dose by up to 37.5%, but insufficiently purified products perform 10–30% worse under optimum conditions and generate 30–300% higher trihalomethane formation potential. Purity, not aluminium yield, is the limiting variable for potable applications.
4. Used as sorbents, aluminium wastes reach 6.7–44.1 mg P/g, up to 30.5–62.4 mg F/g and 14.9–15.9 mg As(V)/g. Capacity is controlled by the amorphous, reactive aluminium fraction and by the point of zero charge rather than by total aluminium content, and the activation route governs whether aluminium leaching from the sorbent is negligible or severe.
5. The sludge examined here is, by the XRF evidence, an unusually favourable feedstock: approximately 71.5% Al2O3 and 24.8% SO3 on an oxide basis, a molar Al/S ratio of 4.53, a

calculated basicity OH/Al of about 2.6, and no detected sodium, magnesium or potassium. Its calculated basicity lies just above the 2.0–2.4 window in which polyaluminium coagulants are manufactured, and the stoichiometric acid demand to enter that window -about 0.21 t H2SO4 per tonne of dry sludge -is roughly six times lower than that required for full conversion to aluminium sulfate.

6. These conclusions about the sample are conditional on the limitations of the analytical method. XRF with fundamental-parameters quantification does not measure oxygen, hydrogen, carbon or nitrogen and normalises the detected elements to 100%; the derived oxide fractions, basicity, notional formula and trace-element estimates are calculated values, not measurements. X-ray diffraction, thermal analysis, ICP determination of trace metals, leaching tests and jar tests with residual-aluminium measurement are required before any performance claim is made.
7. No peer-reviewed study of the valorisation of aluminium-bearing technogenic waste for water treatment in Uzbekistan was identified. That gap, together with the composition reported here, defines a concrete and locally relevant experimental programme.

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