

Stage-Resolved Characterization of Wastewater Sludge Streams for Thermochemical Valorization: Moisture, Fuel Value, and Ash Mineralogy Constraints

Gursel Abbas

gabbas@wisc.edu

University of Wisconsin-Madison <https://orcid.org/0000-0001-7438-8595>

Nazrin Akbarova

Aldevron LLC

Ozge Yuksel Orhan

Hacettepe University: Hacettepe Universitesi <https://orcid.org/0000-0003-0135-0363>

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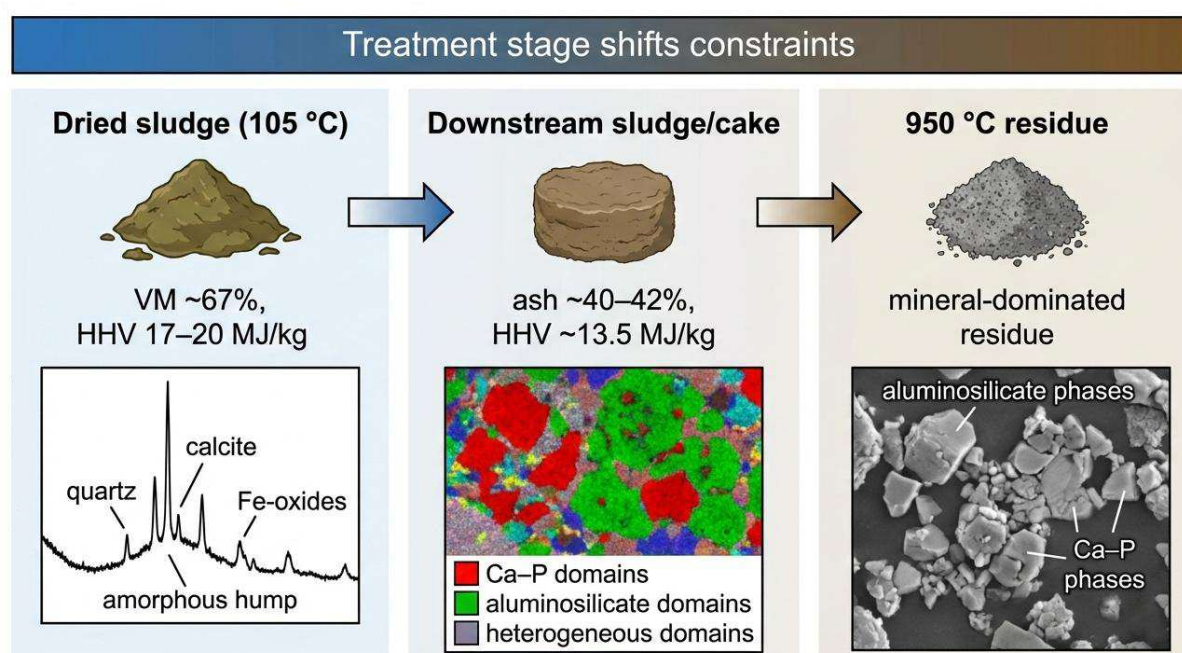
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Stage-Resolved Characterization of Wastewater Sludge Streams for Thermochemical Valorization: Moisture, Fuel Value, and Ash Mineralogy Constraints

Abstract

Wastewater sludges are often treated as a single feedstock in thermochemical studies, despite substantial variations across treatment stages. Five sludge streams from the Ankara Central Wastewater Treatment Plant, primary sludge, waste activated sludge (WAS), raw sludge, anaerobically digested sludge, and dewatered cake were characterized by gravimetric moisture analysis, TGA-based proximate analysis, oxygen bomb calorimetry for higher heating value, XRD of dried solids and 950 °C residues, and SEM/EDS of selected residues. The as-received moisture contents were very high for four sludge streams, exceeding 97%, indicating that drying would be the first practical barrier before thermal conversion. Even after mechanical dewatering, the cake still contained $77.2 \pm 1.4\%$ moisture. On a dry basis, primary sludge, WAS, raw sludge showed similar volatile matter (67%) and lower ash (25-28%), whereas anaerobic sludge and sludge cake had lower volatile matter ($\sim 54\%$) and higher ash (40-42%), with HHV decreasing from 19.9 ± 0.6 MJ/kg (primary) to 13.5-13.6 MJ/kg (anaerobic/cake). Dried sludges showed quartz/calcite/Fe-oxide signatures, with an amorphous contribution; 950 °C residues were mineral-dominated, with aluminosilicate and Ca-P phases and microstructural heterogeneity. Treatment stage shifted the dominant constraint from moisture limited energy recovery in upstream streams to ash and residue limited management in downstream streams. These results demonstrate that sludge should not be treated as a single feedstock class and that thermochemical pathway screening should evaluate moisture burden, dry-basis fuel value, ash loading, and mineral residue behavior together.



Keywords: Municipal biosolids; Proximate analysis; Anaerobic digestion; Bomb calorimetry; X-ray diffraction; Resource recovery

1. Introduction

Municipal wastewater sludges are receiving growing attention as secondary resources for energy recovery and value-added material production [1, 2]. In practice, however, their use is constrained by several feedstock-level issues. Sludge can carry a large water burden, which increases the energy required for drying, while its inorganic fraction can change during thermal treatment and contribute to sintering, slagging, fouling, or other ash-related problems [3–6]. These challenges are not uniform across a treatment plant. Primary sludge, waste activated sludge, digested sludge, and dewatered cake can differ markedly in solids content, organic matter, and mineral fraction, but comparative studies often still group them under the broad label of “sewage sludge” [3, 7]. To address this limitation, this study characterizes multiple sludge streams from different treatment stages using a common analytical protocol designed to define the main constraints on thermochemical processing and residue management.

These constraints are especially relevant in Türkiye, where high-volume municipal residues still require costly handling and are often routed mainly toward disposal. Policies aimed at reducing biodegradable waste in landfills, such as the EU Landfill Directive, support the shift from simple disposal toward resource recovery [8, 9]. Sewage sludge is therefore both a waste-management burden and a locally available feedstock. Its feasibility for energy recovery or material-use pathways cannot be judged from availability alone. Three practical questions must be addressed first: how much water must be removed, how much organic matter remains for conversion, and which mineral phases persist, disappear, or form during heating.

Sewage sludge is produced continuously during municipal and industrial wastewater treatment. In activated sludge systems, waste activated sludge consists mainly of microbial biomass formed as microorganisms metabolize influent organics. The suspended solids are then separated from the treated water [10]. Because sludge contains both biodegradable organic matter and a concentrated inorganic fraction, it has been evaluated as more than a disposal stream. Energy recovery and, in selected cases, higher-value product formation are possible [11]. Interest in these pathways has grown as traditional outlets, including land application and disposal, come under increasing scrutiny because of contaminants, changing regulations, public concerns, and rising management costs [12–14].

The Ankara Central Wastewater Treatment Plant provides a plant scale example. It has a nominal capacity of 765,000 m³ day⁻¹ and treats roughly 250 million m³ annually. Waste activated sludge is thickened, combined with primary sludge, and sent to anaerobic digestion for biogas production. Electricity from this biogas reportedly supplies 80-85% of plant demand, roughly 21 million kWh per year. Centrifuge decanters then increase solids content from about 4-6% to 27-30%. While this reduces transport volume, the material remains water-rich. At 27-30% solids, one ton of dry solids is still associated with 3.3-3.7 tons of wet sludge. Any handling, storage, or thermal conversion route must account for roughly 2.3-2.7 tons of water per ton of dry solids [15].

Water removal is one of the first technical constraints for sludge valorization. Streams leaving treatment units often contain high moisture, which increases transport volume and complicates storage. During thermal conversion, heat is consumed to evaporate water before the solids reach effective conversion temperatures [16, 17]. Mechanical dewatering mitigates this, but sludge cake often retains 68-80% water depending on stabilization, polymer conditioning, and equipment [18]. Acceptable moisture depends on the intended outlet. Levels below 60% may suffice for storage or land-based management, whereas combustion, gasification, and pyrolysis generally require feedstocks below ~15% moisture to maintain stable operation and limit auxiliary fuel use [19].

Dewatering and drying therefore strongly influence technical feasibility, cost, and environmental performance. System-level studies indicate that both drying intensity and the energy source used can dominate the energy and environmental balance of sludge management [20, 21]. Conditioning may involve natural or solar drying, mechanical and thermal drying, or biological approaches using self-heating to accelerate water removal. The selected method must match both the starting solids content and the intended final use [22, 23].

Sewage sludge can contain both organic and inorganic contaminants, so reuse decisions cannot be based only on energy content. Such decisions also require a risk-based assessment that connects the measured sludge composition to the intended outlet [12, 24]. The inorganic fraction is especially important because ash chemistry and trace metals can affect thermal operation, limit land application, and determine whether ash-derived products are acceptable for reuse [25]. In combustion or incineration, mineral composition influences slagging, fouling, and pollutant formation, while regulated gases such as NO_x , SO_x , CO, and, in some cases, N_2O must be managed with appropriate control systems [26, 27].

Full-scale sludge-to-energy systems usually combine dewatering and drying with fluidized-bed combustion or incineration, along with downstream gas cleaning operations. Similar pretreatment strategies are widely used in industrial gas processing systems, where dehydration and contaminant removal are essential before downstream transport or utilization [28]. Some systems also enhance anaerobic digestion. For example, thermal hydrolysis can increase methane production and stabilize solids. Even with strong on-site energy recovery, residual solids remain. These materials still require dewatering, transport, and either disposal or further processing [29, 30].

One reason sludge valorization routes can underperform is that different sludge streams are sometimes treated as if they are interchangeable fuels or feedstocks. In reality, moisture content, ash chemistry, and contaminant profiles can change with both treatment stage and site, and these differences may control conversion behavior, emissions-control requirements, and the possible outlets for products or residues [3, 31, 32]. For this reason, pathway selection should begin with feedstock characterization rather than with an assumed conversion technology. In many cases, the measured properties of the sludge may determine whether a route is practical more strongly than the nominal choice between combustion, gasification, pyrolysis, digestion, or material recovery [32, 33].

The objective of this study is therefore to generate a stage-resolved characterization dataset for several sludge streams from the same wastewater treatment plant, so that potential thermochemical conversion and residue management routes can be screened using measured constraints rather than averaged sewage-sludge assumptions. We measured moisture content, TGA-derived proximate behavior, and higher heating value (HHV), and we used XRD to evaluate crystalline phases before and after heating to 950 °C. SEM/EDS was used on selected high-temperature residues to examine microstructure and elemental heterogeneity. To place the sludge results in a broader fuel context, representative coals and biomasses were analyzed using the same fuel-relevant methods. The resulting dataset is intended as a characterization-first screening framework for sludge-to-energy and sludge-ash management pathways. It is not intended to provide a quantitative life-cycle assessment, but rather to identify the main material constraints that would need to be addressed before process-level evaluation.

Datasets that compare several sludge streams from the same treatment plant remain relatively limited, especially for Türkiye. This gap defines the main contribution of the present work. We do not propose a new conversion unit or claim a validated integrated process. Instead, we provide a decision-oriented characterization

dataset that connects measurable material properties, including moisture content, organic fraction, ash loading, and mineral phase changes, to the practical limits that would affect handling, thermal operation, emissions control, and possible residue-use pathways.

2. Materials and Methods

2.1. Residue sources and stream definitions

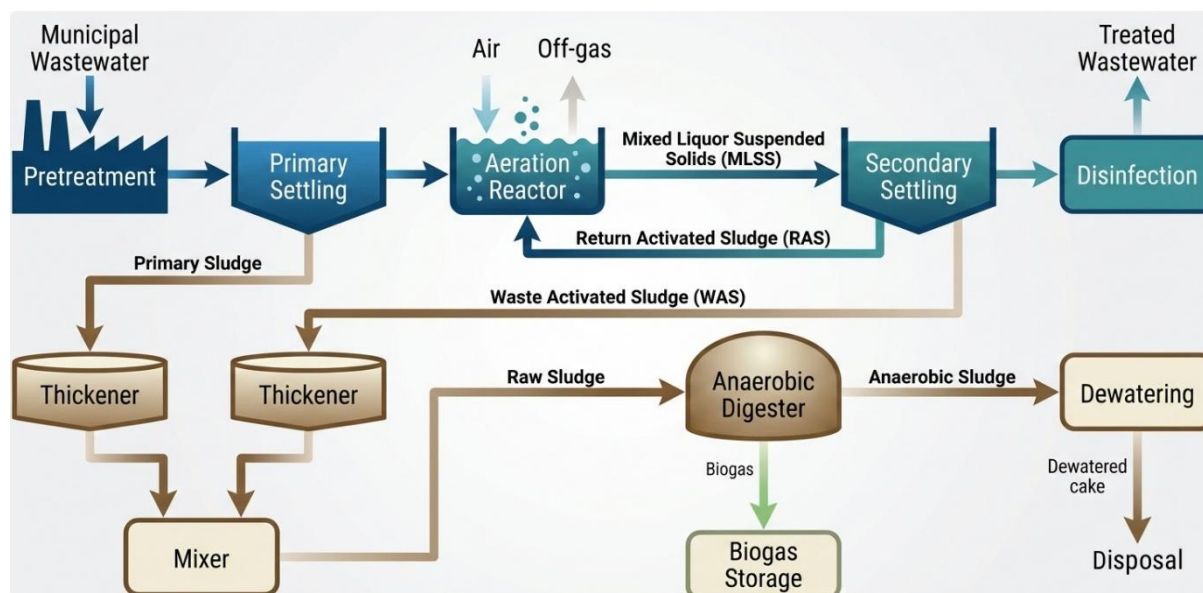


Figure 1. Sludge handling pathway at the Ankara Central Wastewater Treatment Plant, showing the unit operations used to define the five sampling points: primary sludge, waste activated sludge, raw sludge, anaerobic sludge, and dewatered sludge cake.

Five sewage sludge streams were collected from the Ankara Central Wastewater Treatment Plant to represent different points in the sludge handling line (Figure 1). Primary sludge refers to the settled solids removed during primary clarification after preliminary physical treatment. Waste activated sludge (WAS) refers to the excess biological solids removed from the activated-sludge system after aeration and secondary settling. Raw sludge is used here for the thickened mixture of primary sludge and WAS before anaerobic digestion. Anaerobic, or digested, sludge refers to the residual solids obtained after mesophilic anaerobic digestion for biogas production. Sludge cake refers to the mechanically dewatered digested sludge produced before final disposal. These five streams were selected so that changes in moisture, organic content, ash fraction, and residue behavior could be compared across the treatment train rather than inferred from a single bulk “sewage sludge” sample.

Reference fuels and biomass samples were also analyzed to place the sludge results in context. The benchmark set included commercially purchased materials: 11 lignite samples, 15 hard coal samples, 6 coke samples, 2 algal biomass samples, and 7 lignocellulosic or other biomass materials. These samples were not intended to represent local waste streams, but to provide a consistent comparison for proximate composition and higher heating value. All reference materials were prepared and analyzed using the same drying, homogenization, and characterization procedures used for the sludge samples.

2.2. Sample preparation and basis

For analyses reported on a dry basis, subsamples were dried in a convection oven at 105 °C for 6 h. The dried materials were then cooled in a desiccator and stored in airtight containers until analysis. All dry-basis results refer to this 105 °C drying condition. A small loss of highly volatile organic compounds during oven drying cannot be ruled out, but this effect is expected to be minor compared with the mass of water removed and was not distinguishable within the uncertainty of the gravimetric measurements.

2.3. Moisture measurement

Moisture content was measured by drying the as-received samples at 105 °C for 6 h and calculating the mass loss relative to the initial sample mass.

2.4. TGA proximate protocol

Thermogravimetric analysis (TGA) was used to evaluate the proximate behavior of the dried sludge samples and reference fuels/biomass materials. Dried sludge samples were heated to 950 °C under N₂, and volatile matter and ash were determined using a thermogravimetric analyzer following the principles of ASTM D3175, ASTM D3173, and ASTM D3174. Ash content was determined at 550 °C under O₂. Fixed carbon was calculated by difference from moisture, volatile matter, and ash. Operating parameters that can affect TGA outputs, including sample mass, heating rate, purge gas composition, purge flow rate, and hold time, are provided in the Supporting Information.

2.5. Higher heating value (HHV) measurement

The higher heating value (HHV) of dried sludge samples and reference fuels/biomass materials was measured using a LECO AC-350 oxygen bomb calorimeter. Pre-weighed subsamples were combusted under 30 atm O₂ according to the manufacturer's protocol and standard bomb-calorimetry practice. HHV values are reported on a dry basis.

2.6. Ash preparation at 950 °C and XRD protocols

Ash/residue samples from the five sludge types were prepared by heating dried samples to 950 °C for 30 min in a muffle oven. The resulting ash/residue fractions were collected and characterized to evaluate inorganic phases and morphology relevant to ash management and potential secondary use. Crystalline phases in dried sludge samples and their corresponding ash/residue fractions were identified by X-ray diffraction (XRD). XRD scan conditions are provided in the Supplementary Material.

2.7. SEM/EDS conditions and quantification basis

Microstructural characterization was performed by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). SEM imaging and EDS mapping/spot analyses were conducted for primary sludge ash and sludge cake ash to evaluate morphology, particle structure, and elemental distributions after high-temperature treatment. SEM operating conditions (accelerating voltage, working distance, detector configuration), sample mounting, and any conductive coating are reported in the Supplementary Material. EDS results are interpreted as semi-quantitative.

2.8. Statistics and replicates

Sludge measurements were performed in triplicate ($n = 3$), whereas reference fuels/biomass materials were analyzed in duplicate ($n = 2$). Results are reported as mean $\pm$ standard deviation (SD). For derived quantities, the calculation basis and equations are provided in the relevant subsection and/or in the Supplementary Material.

3. Results

3.1. Feedstock properties of five sludge streams

All five sludge streams contained a large amount of water in the as-received state, confirming that handling and drying would be major practical issues before any valorization step. Primary sludge, WAS, raw sludge, and anaerobic sludge each had moisture contents above 97% (Table 1). Sludge cake was the only stream with substantially lower moisture, $77.2 \pm 1.4\%$, and correspondingly higher total solids, $22.8 \pm 1.4\%$, because it had already passed through mechanical dewatering (Table 1, S1, and S2). After the laboratory pre-drying step at $105\text{ }^{\circ}\text{C}$ for 6 h, the remaining moisture in all sludge samples decreased to low single-digit values, approximately 1.7-3.8% (Table S3). This provided a consistent dried basis for the subsequent proximate, HHV, and solid-phase analyses.

Table 1. As-received moisture, total solids, and dry-basis higher heating value of the five Ankara sludge streams. Values are reported as mean $\pm$ SD from triplicate measurements ($n = 3$). HHV was measured by oxygen bomb calorimetry and is reported on a dry basis. Replicate values are provided in Table S1, S2 and S10.

	Moisture content (%)	Total solids (%)	HHV (MJ/kg)
Primary sludge	97.4 ± 1.1	2.6 ± 1.1	19.9 ± 0.6
Waste Activated Sludge	98.9 ± 0.7	1.1 ± 0.7	17.2 ± 0.5
Raw sludge	97.6 ± 1.3	2.4 ± 1.3	18.3 ± 0.6
Anaerobic sludge	98.4 ± 1.1	1.7 ± 1.1	13.5 ± 0.4
Sludge cake	77.2 ± 1.4	22.8 ± 1.4	13.6 ± 0.4

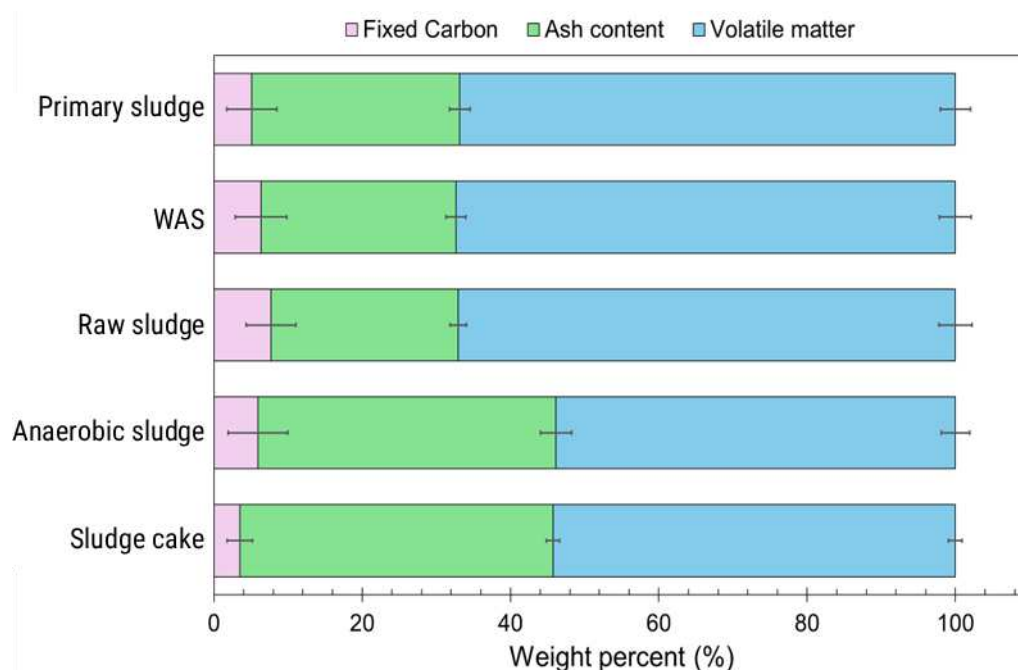


Figure 2. TGA-derived proximate behavior of the Ankara sludge streams on a dry basis. Volatile matter, ash, and fixed carbon are reported as mean $\pm$ SD ($n = 3$). Fixed carbon was calculated by difference using the dry-basis volatile matter and ash content determined by TGA: $FC = 100 - (VM + Ash_{550})$ where FC is fixed carbon (dry, wt%), VM is volatile matter (dry, wt%), and Ash_{550} is ash measured at 550 °C (dry, wt%). The numerical values used to generate the figure are provided in Tables S5, S6, S7, and S8.

The HHV results followed the same pattern observed in the proximate analysis and further separated the sludge streams in terms of dry-basis energy content (Table 1). Primary sludge had the highest HHV, followed by raw sludge and WAS. In contrast, anaerobic sludge and sludge cake showed clearly lower HHV values, which is consistent with their lower volatile matter contents and higher ash fractions after digestion and downstream dewatering (Figure 2).

3.2. Benchmark comparison with solid fuels and biomasses

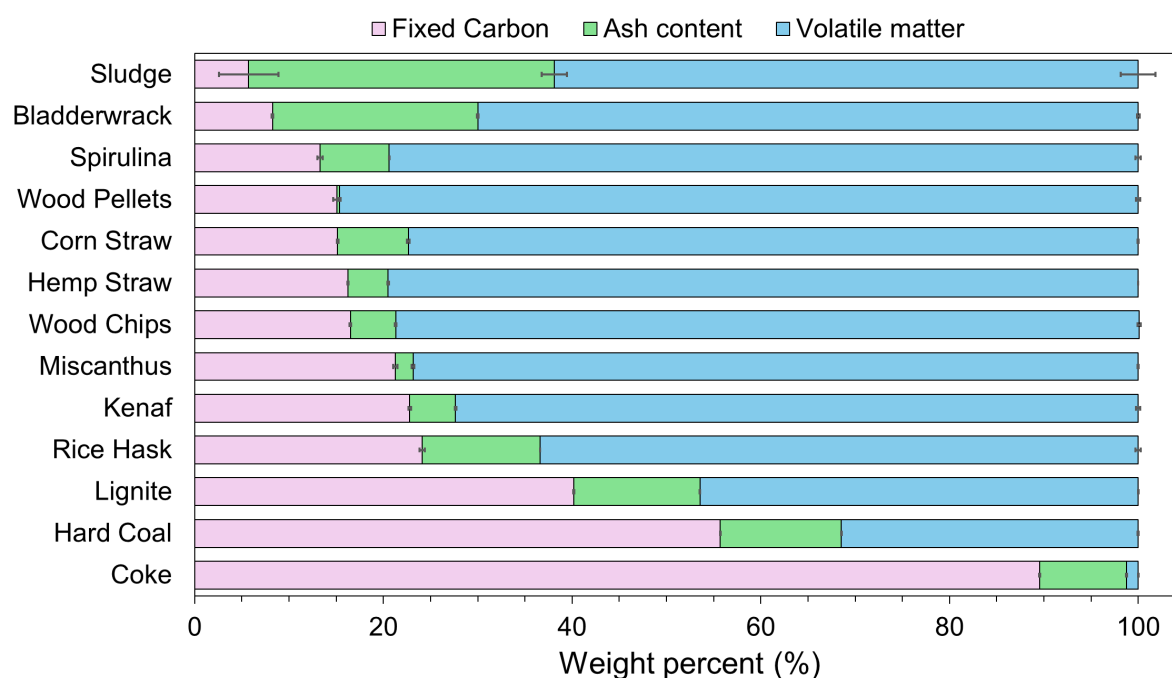


Figure 3. Comparative proximate composition of Ankara sludge, benchmark solid fuels, and biomass reference materials. Values are reported on a dry wt% basis as volatile matter, ash, and fixed carbon. The sludge value represents the mean of the five Ankara sludge streams. Lignite, hard coal, and coke represent mean values for the purchased benchmark samples, with $n = 11$, $n = 15$, and $n = 6$, respectively. The algal and lignocellulosic biomass samples were analyzed as reference materials using the same protocol. Volatile matter and ash were determined by TGA. Fixed carbon was calculated by difference using $\text{Fixed carbon} = 100 - (\text{volatile matter} + \text{Ash}_{550})$, where Ash_{550} is the ash content measured at 550 °C. Numerical values are provided in Table S4 and S9.

Comparing Ankara sludge with common solid fuels and reference biomasses highlights why ash management is a critical consideration in sludge-to-energy applications (Figure 3). On a dry basis, the average ash content of the sludge samples was 32.4%, far higher than the lignocellulosic biomasses measured here, which ranged from 0.3-7.5%, and also above the average values for lignite and hard coal, 13.4% and 12.8%, respectively. Sludge also exceeded coke in ash content, 9.2%, although coke is fundamentally different because its proximate composition is dominated by fixed carbon. The fixed-carbon fraction in sludge was only 5.7%, compared with 40.2% for lignite, 55.7% for hard coal, and 89.6% for coke. This low fixed-carbon fraction indicates that most of the combustible portion of sludge comes from volatile matter rather than char burnout. The average volatile matter content, 61.9%, was slightly below most lignocellulosic biomasses in the benchmark set, approximately 63-85%, but well above hard coal, 31.5%, and coke, 1.2%. These comparisons show that sludge should not be treated as a coal-like fixed-carbon fuel. It is better described as a volatile-rich, high-ash residue, where handling of the mineral fraction can be as important as organic conversion.

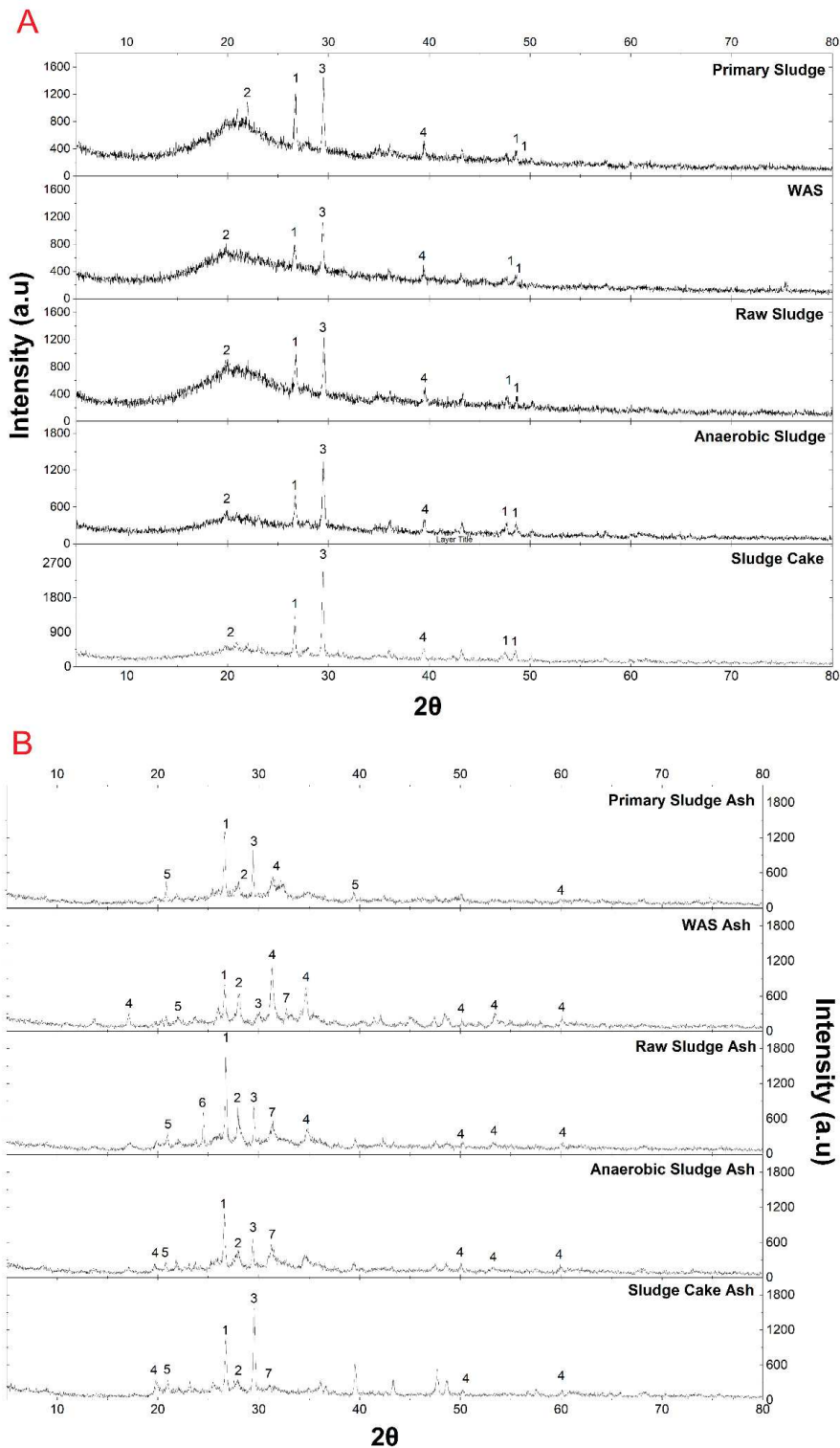
The HHV values of the sludge samples were compared with those of benchmark fuels and selected lignocellulosic and algal biomasses using the same bomb-calorimetry protocol (Table 2). Fossil-derived fuels had the highest energy densities, with coke at 27.6 ± 0.4 MJ/kg and hard coal at 24.0 ± 0.0 MJ/kg, consistent with their higher carbon content and lower oxygen content. Lignite and wood pellets showed intermediate values, 19.3

± 0.2 and 19.2 ± 0.2 MJ/kg, respectively. The average sludge HHV was 16.5 ± 0.5 MJ/kg, placing it near the upper end of the lignocellulosic residues measured in this study, including rice husk and herbaceous or woody biomasses, which ranged from 14.9 to 16.3 MJ/kg. On a dry basis, after moisture removal, sludge approaches the energy content of some agricultural residues. Corresponding moisture values are provided in Table S5. Algal biomasses showed broader variability: Spirulina had a relatively high HHV of 20.9 ± 0.3 MJ/kg, while bladderwrack was lower at 13.2 ± 0.1 MJ/kg. This variation indicates that HHV in biomass-type materials is primarily influenced by biochemical composition and ash content, rather than by the broad classification as “biomass.”

Table 2. Dry-basis higher heating values (HHV) for sludge, benchmark solid fuels, and biomass reference materials determined by oxygen bomb calorimetry. Data are shown as mean ± SD. Benchmark fuels and biomass materials were analyzed in duplicate (n = 2), and sludge samples were analyzed in triplicate (n = 3). Replicate measurements are listed in Table S11.

Sample	HHV (MJ/kg)	Sample	HHV (MJ/kg)
Coke	27.6 ± 0.4	Corn Straw	16.3 ± 0.2
Hard Coal	24.0 ± 0.0	Hemp Straw	15.8 ± 0.1
Spirulina	20.9 ± 0.3	Kenaf	15.6 ± 0.2
Lignite	19.3 ± 0.2	Miscanthus	15.5 ± 0.0
Wood Pellets	19.2 ± 0.2	Rice Husk	14.9 ± 0.1
Sludge	16.5 ± 0.5	Bladderwrack	13.2 ± 0.1
Wood Chips	16.3 ± 0.2		

243 3.3. Mineral phase changes and residue heterogeneity



244
 245 *Figure 4. A.* XRD patterns of Ankara sludge streams dried at 105 °C for 6 h. Numbered peaks indicate (1) calcite,
 246 CaCO_3 ; (2) amorphous or poorly crystalline material shown by the diffuse background; (3) quartz, SiO_2 ; and (4)
 247 Fe-oxide-related phases, including Fe_2O_3 /Fe-oxide reflections. **B.** XRD patterns of sludge ash/residue generated
 248 by heating dried Ankara sludge streams to 950 °C for 30 min in a muffle oven. Assigned phases include: (1) quartz,
 249 SiO_2 ; (2) albite, $\text{NaAlSi}_3\text{O}_8$; (3) carbonate-related reflections, such as calcite; (4) merrillite, $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$; (5)
 250 alumina, Al_2O_3 ; (6) K-feldspar, KAlSi_3O_8 ; and (7) carbonate-related reflections, such as dolomite.

The XRD patterns in *Figure 4* indicate that the oven-dried sludge samples contained a mix of crystalline and poorly ordered material. Across all five sludge streams, the main crystalline reflections were identified as quartz, calcite, and Fe-oxide-bearing phases. These reflections were superimposed on a broad diffuse signal at approximately $15\text{-}30^\circ 2\theta$, indicating that much of the dried solid matrix remained amorphous or only weakly crystalline. This is expected for wastewater-derived solids, which contain mixed organic, biological, and inorganic material rather than a single well-defined mineral phase. Compared with primary sludge, WAS, and raw sludge, the anaerobic sludge and sludge cake show a less pronounced diffuse background and more mineral-dominated patterns. This agrees with the proximate results, where downstream treatment reduced the organic fraction and increased the relative contribution of inorganic material.

After heating to 950°C , the XRD patterns became much more strongly controlled by mineral phases, as expected after removal of most organic matter (*Figure 4*). Quartz was still present in the residues from all sludge streams. The patterns also showed reflections consistent with aluminosilicate phases, including $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 , together with Al_2O_3 and Ca-P minerals such as merrillite, $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$. These results indicate that high-temperature treatment converts the sludge solids into a residue matrix dominated by silicate-, aluminosilicate-, and phosphate-bearing components. Any carbonate-related reflections should be treated with caution, because carbonates are not expected to be fully stable at 950°C and may also form or change during cooling and exposure after the heating step.

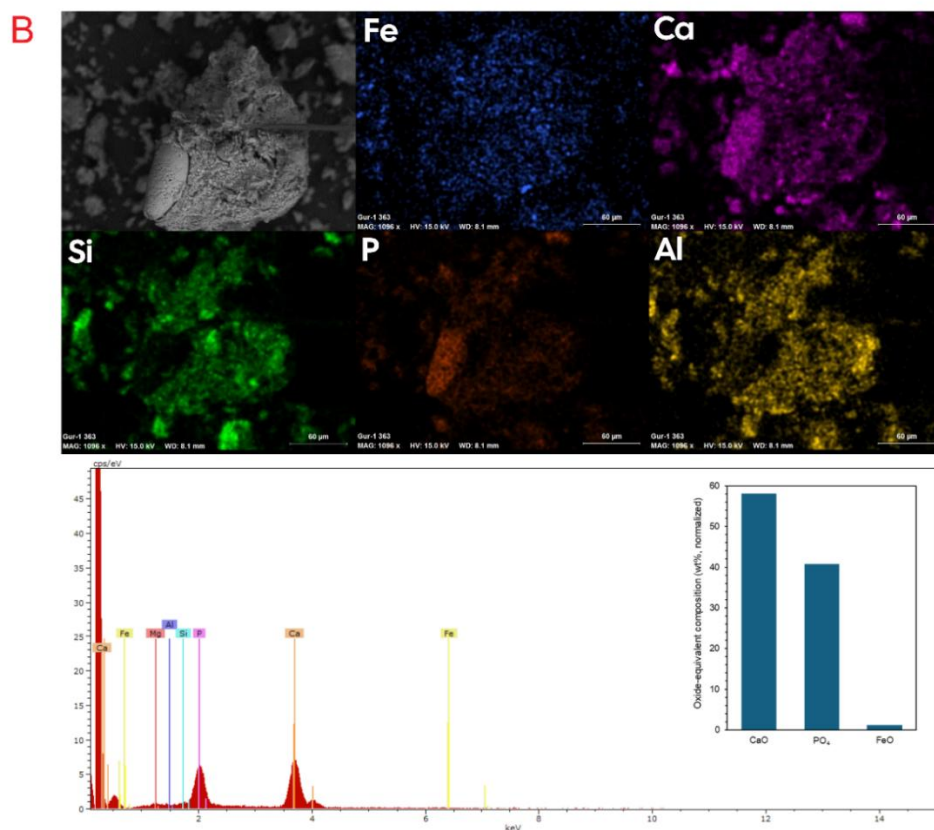
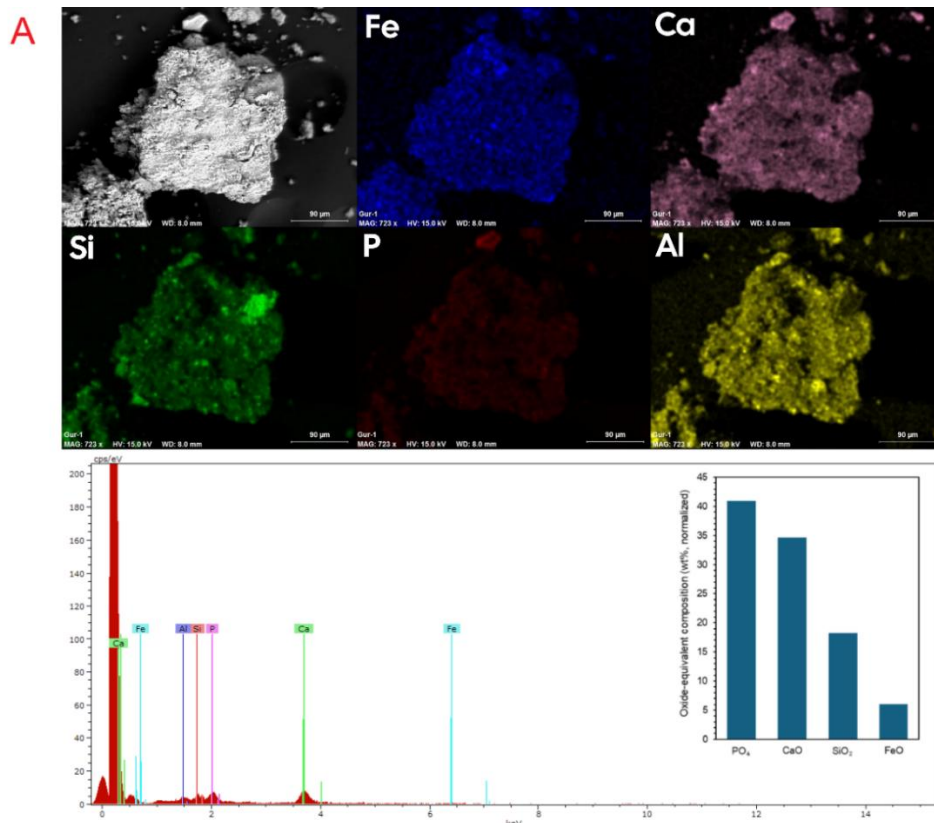


Figure 5. A. SEM-EDS elemental maps of primary sludge residue prepared by heating the dried sample to 950 °C for 30 min in a muffle oven; B. SEM-EDS elemental maps of sludge cake residue prepared by heating the dried sample to 950 °C for 30 min in a muffle oven.

SEM imaging and SEM-EDS mapping were used to examine the mineral residue formed after heating selected sludge samples to 950 °C. The primary sludge residue was used as a representative early-stage sample, while sludge cake was used as a downstream, dewatered sample (Figure 5). Both residues contained angular agglomerates and partially fused regions, suggesting that the inorganic particles had sintered or coalesced during high-temperature treatment. The textures were not uniform, which is consistent with a mixed mineral residue rather than a single homogeneous ash phase. In the primary sludge residue, the elemental maps show Ca- and P-rich areas together with separate Si- and Al-containing regions. This suggests that Ca-P-rich phases are present alongside silica or aluminosilicate particles. Point EDS analysis, reported using oxide-equivalent normalization, also showed large PO₄ and CaO contributions, 40.98 wt% and 34.66 wt%, respectively, together with SiO₂ at 18.27 wt% and a smaller FeO_x contribution reported as FeO at 6.09 wt%. These SEM-EDS results are consistent with the XRD patterns, which showed quartz together with phosphate-bearing and aluminosilicate phases in the 950 °C residues.

The sludge cake residue showed a stronger Ca-P signature at the particle scale after heating to 950 °C. In the mapped agglomerate, Ca and P were distributed across much of the analyzed area, whereas Si and Al were less pronounced in this field of view. This suggests that the local chemistry of the sludge cake residue is dominated by Ca-P-rich material, with smaller contributions from silicate or aluminosilicate phases. The point EDS analysis supports this observation, showing 58.13 wt% CaO and 40.74 wt% PO₄ on an oxide-equivalent basis, with only a minor FeO_x contribution reported as FeO at 1.12 wt%. When combined with the mineral-dominated XRD patterns of the incinerated residues (Figure 4), the SEM-EDS maps indicate that high-temperature treatment reorganized the inorganic fraction into Ca-P-rich domains, along with accompanying silicate and aluminosilicate components. This Ca-P enrichment was more pronounced in the downstream sludge cake residue than in the primary sludge residue within the analyzed regions (Figure 5).

4. Discussion

The combined moisture, TGA-derived proximate behavior, HHV, and solid-phase characterization results provide a stage-resolved view of how the Ankara wastewater treatment train shifts sludge from an energy-bearing organic residue toward an increasingly mineral-dominated material. The upstream streams retain more organic material and therefore higher dry-basis fuel value, whereas the downstream digested sludge and sludge cake become more mineral-rich as organic matter is stabilized and ash is concentrated [3, 34]. At the same time, dry-basis fuel quality alone does not determine whether a sludge stream is practical for thermal conversion. For the early-stage streams, the very high as-received moisture content creates the main handling and energy penalty, so dewatering and drying become the first constraints that must be solved [3, 22, 34]. In the present dataset, however, the treatment stage changes the controlling question from simply “how much energy does the dry material contain?” to “how much water and mineral matter must be managed before that energy can be used” [3, 11, 34].

The TGA results show clear changes in the organic and inorganic fractions across the sludge treatment train (Figure 2). On a dry basis, primary sludge, WAS, and raw sludge had very similar volatile matter contents, 66.8 ± 2.1%, 67.3 ± 2.1%, and 67.1 ± 2.2%, respectively. The close agreement among these values indicates that the upstream and blended streams retained a similar pool of thermally labile organic material. Following anaerobic digestion, this pool was reduced, with anaerobic sludge and sludge cake showing volatile matter contents of 53.9 ± 1.9% and 54.3 ± 0.9%, respectively. The decline is consistent with biological stabilization, during which a

portion of the readily degradable organic fraction is converted during digestion. Ash content shifted in the opposite direction. Primary sludge, WAS, and raw sludge contained $28.1 \pm 1.4\%$, $26.3 \pm 1.4\%$, and $25.2 \pm 1.1\%$ ash at 550 °C, while anaerobic sludge and sludge cake increased to $40.2 \pm 2.1\%$ and $42.2 \pm 0.9\%$, respectively. Fixed carbon, calculated by difference from volatile matter and ash at 550 °C, was low in all samples, ranging from $3.5 \pm 1.7\%$ for sludge cake to $7.7 \pm 3.3\%$ for raw sludge.

Overall, the proximate analysis indicates that the combustible portion of these sludges is mainly associated with volatile release rather than fixed-carbon burnout (Figure 2). Primary sludge, WAS, and raw sludge have nearly the same volatile matter content on a dry basis, whereas anaerobic sludge and sludge cake show a clear loss of volatile matter together with a higher ash fraction. This pattern is expected after biological treatment. Anaerobic digestion removes part of the readily convertible organic material, while the inorganic fraction is largely retained and therefore becomes more concentrated as the organic pool decreases [3, 11, 35]. For thermal conversion, this means that the downstream samples are not only “lower energy” materials; they are also different types of feedstocks from an operating perspective. Because fixed carbon was low in all streams, conversion performance is likely to be governed less by char burnout than by the rate and completeness of volatile release, mixing, and oxidation or secondary conversion within the available residence time. The higher ash contents of anaerobic sludge and sludge cake also shift the downstream samples toward a more mineral-constrained operating regime. Reactor design would therefore have to provide sufficient heat transfer and residence time for volatile conversion while also limiting ash deposition, sintering, and corrosion, particularly where Ca-, P-, and alkali-associated phases are involved [1, 3, 35].

The 950 °C residue measurements followed the same general trend as the ash contents measured at 550 °C, but the remaining fraction was slightly lower for each sludge stream (Figure S1). For primary sludge, the ash content was $28.1 \pm 1.4\%$ at 550 °C, while the residue after heating to 950 °C decreased to $26.5 \pm 1.4\%$. This small loss comes from additional decomposition of inorganic components at higher temperatures.

The proximate and HHV results show that the earlier-stage sludges, primary sludge, WAS, and raw sludge, retain higher dry-basis energy content, while the downstream sludge cake is more mineral-rich and therefore more diluted as a fuel. The HHV values in Table 1 suggest that part of the apparent energy loss along the treatment train is related to ash enrichment rather than only to a change in the quality of the remaining organic material. On a dry basis, the early-stage sludges have HHVs that are similar to, or higher than, several lignocellulosic residues included in the benchmark set (Figure 3). By contrast, anaerobic sludge and sludge cake decrease to the low teens in MJ/kg, consistent with their higher ash contents. However, these dry-basis values cannot be interpreted alone. Primary sludge, WAS, raw sludge, and anaerobic sludge all contain extremely high moisture in the as-received state (Table 1), so any energy-recovery route would first have to overcome a large drying and handling burden [22, 34, 36]. Sludge cake has a lower dry-basis HHV, but it may still be more practical to process because it starts at a much higher solids content. From an operational standpoint, the preferred stream is therefore not automatically the one with the highest dry-basis calorific value, but the one that offers the most workable balance among recoverable chemical energy, moisture removal, and ash loading [24, 37]. HHV should therefore be treated as only one screening metric. It should evaluate each sludge stream using paired indicators that capture both the dry-basis energy content and the water and mineral matter that must be managed before that energy can be recovered [34, 37].

The purchased coals, coke, and representative biomasses provide a reference frame for evaluating sludge as a fuel-like material [3, 34]. On a dry basis, the average sludge HHV lies near the upper end of several agricultural and woody residues, indicating that energy recovery is plausible in principle [34]. Proximate composition, however, shows why HHV is not sufficient for screening. Sludge contains far more ash than most lignocellulosic feedstocks, which makes ash management a core design constraint rather than a secondary residue-handling issue [3, 34, 38]. In a thermal system, this would likely translate into greater solids throughput per unit of recovered energy, increased risk of inorganic-driven deposition or corrosion, and a stronger need to define acceptable ash reuse or disposal pathways [38–40]. Assumptions based on low-ash biomass systems cannot be applied to sludge without considering its mineral content and ash chemistry. Even feedstocks with similar HHV values can behave very differently if their inorganic fractions vary [39–41].

The XRD and SEM-EDS results indicate that solid residue is a primary constraint in sludge valorization, not a secondary by-product. In the dried sludge samples, quartz, calcite, and Fe-oxide-bearing phases occurred together with a broad amorphous background, reflecting the mixed organic-inorganic character of wastewater-derived solids. After treatment at 950 °C, the residues became increasingly mineral-dominated. The emergence of aluminosilicate and Ca-P mineral signatures suggests that the inorganic fraction was reorganized during high-temperature exposure into more crystalline and thermally persistent assemblages [34, 42]. The SEM-EDS maps further show that these residues are compositionally heterogeneous. Ca-P-rich regions coexist with silica- or aluminosilicate-rich domains, and the analyzed sludge cake residue showed a stronger Ca-P signature than the primary sludge residue. This particle-scale heterogeneity matters for downstream use because different mineral domains may support different recovery or material-use pathways. Silicate- and aluminosilicate-rich fractions may be relevant to mineral additive applications, whereas Ca-P-rich regions may be more relevant to phosphorus recovery concepts [43, 44]. These observations should still be treated as screening evidence rather than proof of end-use suitability. Any beneficial-use pathway would require trace-metal profiling, leaching assessment, and comparison with the applicable environmental or product standards [42, 45]. More broadly, sludge ash/residue should not be represented as a chemically uniform material in process or system-level assessments. Local phase enrichment and segregation may influence environmental behavior, including element mobility, as well as processing behavior, including sintering, even when bulk composition appears similar [45, 46].

5. Conclusion

This study shows that wastewater sludge should not be treated as one uniform feedstock category. Using a side-by-side dataset from the Ankara treatment train, we found that each treatment stage introduces a different set of constraints for high-temperature valorization. The earlier-stage sludges had higher dry-basis volatile matter and HHV, showing that they still contain meaningful energy potential. However, their very high as-received moisture means that water removal would be the first and most important practical limitation. In contrast, downstream stabilization and dewatering reduced the water content but increased the relative mineral fraction. As a result, the digested sludge and sludge cake had lower dry-basis HHV and higher ash production, making ash handling and inorganic-driven behavior more important for process design.

The solid-phase analyses further show that inorganic residue behavior is a central constraint in sludge valorization. In the dried sludge samples, XRD identified quartz, calcite, and Fe-oxide-bearing phases together with a broad amorphous contribution. After heating to 950 °C, the residues became strongly mineral-dominated

and contained aluminosilicate and Ca-P-bearing phases. SEM-EDS mapping showed clear particle-scale heterogeneity in the heated residues. Ca-P-rich regions occurred together with silica- or aluminosilicate-rich areas, suggesting that different mineral domains may need to be considered separately in future mineral-use or phosphorus-recovery screening. These observations are still only screening-level evidence. Practical use of the ash would require contaminant profiling, leaching assessment, and comparison with the relevant environmental or product standards.

The results show that screening based on material constraints is more informative than relying on fuel value alone. Dry-basis HHV must be considered alongside the water that must be removed before conversion and the mineral fraction that will remain afterward. Benchmark comparisons show that some sludge streams have dry-basis energy contents approaching those of lignocellulosic residues. However, this similarity is limited because the high moisture content and elevated ash fractions of sludge make it operationally distinct from conventional biomass fuels. For practical process design, dewatering performance and ash management should therefore be treated as primary constraints rather than secondary considerations.

This material-screening approach could be expanded toward validation through reactor scale experiments, process modeling, contaminant analysis, and leaching tests. Those steps are necessary to determine whether the observed moisture, energy, ash, and phase-behavior indicators translate into acceptable net efficiency, stable operation, and realistic residue use pathways. The dataset can help prioritize which thermal pathways are worth testing further and which validation measurements are needed before deployment.

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Data Availability

The datasets generated and/or analyzed during the current study are available in the Supplementary Material accompanying this article.

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Conflict of Interest

The authors declare no conflicts of interest.

Reference list

1. Nkuna SG, Olwal TO, Chowdhury SD, Ndambuki JM (2024) A review of wastewater sludge-to-energy generation focused on thermochemical technologies: An improved technological, economical and socio-environmental aspect. *Cleaner Waste Systems* 7:100130. <https://doi.org/10.1016/j.clwas.2024.100130>
2. Pelagalli V, Langone M, Matassa S, Race M, Tuffi R, Papirio S, Lens PNL, Lazzazzara M, Frugis A, Petta L, Esposito G (2024) Pyrolysis of municipal sewage sludge: challenges, opportunities and new valorization routes for biochar, bio-oil, and pyrolysis gas. *Environ Sci: Water Res Technol* 10:2282–2312. <https://doi.org/10.1039/D4EW00278D>
3. Rijo B, Nobre C, Brito P, Ferreira P (2024) An Overview of the Thermochemical Valorization of Sewage Sludge: Principles and Current Challenges. *Energies* 17:2417. <https://doi.org/10.3390/en17102417>
4. Brandstätter G, Fürsatz K, Long A, Hannl TK, Schubert T (2025) Exploring the potential of sewage sludge for gasification and resource recovery: A review. *Environmental Technology & Innovation* 40:104346. <https://doi.org/10.1016/j.eti.2025.104346>
5. Yu Y, Yu Z, Xu W, Zhang K, Tang Y, Cheng G, He X, Dai B (2024) High-Temperature Ash Melting and Fluidity Behavior upon the Cocombustion of Sewage Sludge and Coal. *ACS Omega* 9:14455–14464. <https://doi.org/10.1021/acsomega.4c00227>
6. Falk J, Hannl TK, Öhman M, Hedayati A, Skoglund N (2023) Ash Transformation during Fixed-Bed Cocombustion of Sewage Sludge and Agricultural Residues with a Focus on Phosphorus. *ACS Omega* 8:13162–13176. <https://doi.org/10.1021/acsomega.3c00415>
7. Abdelrahman AM, Kosar S, Gulhan H, Cicekalan B, Ucas G, Atli E, Guven H, Ozgun H, Ozturk I, Koyuncu I, Van Lier JB, Voleke EIP, Ersahin ME (2023) Impact of primary treatment methods on sludge characteristics and digestibility, and wastewater treatment plant-wide economics. *Water Research* 235:119920. <https://doi.org/10.1016/j.watres.2023.119920>
8. EUR-Lex (2024) Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste
9. European Environment Agency (2025) Turkey profile on municipal and packaging waste management - 2025
10. Shi S, Xu G, Yu H, Zhang Z (2018) Strategies of valorization of sludge from wastewater treatment. *J of Chemical Tech & Biotech* 93:936–944. <https://doi.org/10.1002/jctb.5548>
11. Zhang Q, Hu J, Lee D-J, Chang Y, Lee Y-J (2017) Sludge treatment: Current research trends. *Bioresource Technology* 243:1159–1172. <https://doi.org/10.1016/j.biortech.2017.07.070>
12. Braine MF, Kearnes M, Khan SJ (2024) Quality and risk management frameworks for biosolids: An assessment of current international practice. *Science of The Total Environment* 915:169953. <https://doi.org/10.1016/j.scitotenv.2024.169953>
13. Leino O, Äystö L, Fjäder P, Perkola N, Lehtoranta S (2025) Contaminants of environmental concern in sewage sludge in the Nordic countries. *Environmental Pollution* 381:126604. <https://doi.org/https://doi.org/10.1016/j.envpol.2025.126604>
14. Council of the EU (2024) Urban wastewater: Council adopts new rules for more efficient treatment
15. ASKI (2023) Ankara Merkezi Atıksu Arıtma Tesisi. In: ASKI. <https://www.aski.gov.tr/tr/icerikdetay/tatlar-atıksu-arıtma-tesisi/30/22>. Accessed 24 Dec 2025

16. Abbas G, Yuksel Orhan O (2024) Energy penalties of CO₂ storage and transportation. In: *Advances and Technology Development in Greenhouse Gases: Emission, Capture and Conversion*. Elsevier, pp 187–216
17. Wang Q, Wei W, Gong Y, Yu Q, Li Q, Sun J, Yuan Z (2017) Technologies for reducing sludge production in wastewater treatment plants: State of the art. *Science of The Total Environment* 587–588:510–521. <https://doi.org/10.1016/j.scitotenv.2017.02.203>
18. An-nori A, Ezzariai A, El Mejahed K, El Fels L, El Gharous M, Hafidi M (2022) Solar Drying as an Eco-Friendly Technology for Sewage Sludge Stabilization: Assessment of Micropollutant Behavior, Pathogen Removal, and Agronomic Value. *Front Environ Sci* 10:814590. <https://doi.org/10.3389/fenvs.2022.814590>
19. Zhang X-P, Zhang C, Li X, Yu S-H, Tan P, Fang Q-Y, Chen G (2018) A two-step process for sewage sludge treatment: Hydrothermal treatment of sludge and catalytic hydrothermal gasification of its derived liquid. *Fuel Processing Technology* 180:67–74. <https://doi.org/10.1016/j.fuproc.2018.08.012>
20. Karadirek IE, Erkaya O, Ciggin AS (2025) Comparative life cycle assessment of sewage sludge drying by solar and thermal drying technologies. *Waste Management* 201:114826. <https://doi.org/https://doi.org/10.1016/j.wasman.2025.114826>
21. Wang Z, Li X, Liu H, Li J, Vodnar DC, Lin CSK, Wang Q (2024) Life cycle assessment of traditional and innovative sludge management scenarios in Australia: Focusing on environmental impacts, energy balance, and economic benefits. *Resources, Conservation and Recycling* 204:107496. <https://doi.org/https://doi.org/10.1016/j.resconrec.2024.107496>
22. Collard M, Teychené B, Lemée L (2017) Comparison of three different wastewater sludge and their respective drying processes: Solar, thermal and reed beds – Impact on organic matter characteristics. *Journal of Environmental Management* 203:760–767. <https://doi.org/10.1016/j.jenvman.2016.05.070>
23. Zhang C, Li Y, Yu Z, Liu Y, Dong L (2024) Effectiveness of biological drying for citric acid dewatered sludge: Evaluating the impact of energy-efficient ventilation strategies. *Waste Management* 182:237–249. <https://doi.org/https://doi.org/10.1016/j.wasman.2024.04.038>
24. Raheem A, Sikarwar VS, He J, Dastyar W, Dionysiou DD, Wang W, Zhao M (2018) Opportunities and challenges in sustainable treatment and resource reuse of sewage sludge: A review. *Chemical Engineering Journal* 337:616–641. <https://doi.org/10.1016/j.cej.2017.12.149>
25. Wickham R, Xie S, Galway B, Bustamante H, Nghiem LD (2018) Anaerobic digestion of soft drink beverage waste and sewage sludge. *Bioresource Technology* 262:141–147. <https://doi.org/10.1016/j.biortech.2018.04.046>
26. Dong Y, Wang L, Wang F, Zou B, Lv G, Cui H, Ye Z (2024) N₂O emission factors in bubbling fluidized bed incineration of municipal sewage sludge: The China case. *Waste Management* 183:253–259. <https://doi.org/10.1016/j.wasman.2024.05.022>
27. Martin JJE, Koralewska R, Wohlleben A (2015) Advanced solutions in combustion-based WtE technologies. *Waste Management* 37:147–156. <https://doi.org/10.1016/j.wasman.2014.08.026>
28. Hamdan RA, Okmen Altas B, Abbas G, Topcu G, Goktas C, Yavas SG, Kirac E, Yuksel Orhan O (2025) Hydrotreating and Acidic Gas Removal for Natural Gas Pretreatment. In: *Comprehensive Methanol Science*. Elsevier, pp 1–17
29. Swann L, Downs D, Waye M (2017) Waste to Energy Solution – The Sludge Treatment Facility in Tuen Mun, Hong Kong. *Energy Procedia* 143:500–505. <https://doi.org/10.1016/j.egypro.2017.12.717>

30. Azizi SMM, Haffiez N, Mostafa A, Hussain A, Abdallah M, Al-Mamun A, Bhatnagar A, Dhar BR (2024) Low- and high-temperature thermal hydrolysis pretreatment for anaerobic digestion of sludge: Process evaluation and fate of emerging pollutants. *Renewable and Sustainable Energy Reviews* 200:114453. <https://doi.org/10.1016/j.rser.2024.114453>
31. Lucia C, Badalucco L, Corsino SF, Galati A, Iovino M, Muscarella SM, Paliaga S, Torregrossa M, Laudicina VA (2025) Management and valorisation of sewage sludge to foster the circular economy in the agricultural sector. *Discover Soil* 2:80. <https://doi.org/10.1007/s44378-025-00105-9>
32. Giwa AS, Maurice NJ, Luoyan A, Liu X, Yunlong Y, Hong Z (2023) Advances in sewage sludge application and treatment: Process integration of plasma pyrolysis and anaerobic digestion with the resource recovery. *Heliyon* 9:e19765. <https://doi.org/10.1016/j.heliyon.2023.e19765>
33. Chan WP, Wang J-Y (2016) Comprehensive characterisation of sewage sludge for thermochemical conversion processes – Based on Singapore survey. *Waste Management* 54:131–142. <https://doi.org/10.1016/j.wasman.2016.04.038>
34. Gao N, Kamran K, Quan C, Williams PT (2020) Thermochemical conversion of sewage sludge: A critical review. *Progress in Energy and Combustion Science* 79:100843. <https://doi.org/10.1016/j.pecs.2020.100843>
35. Hu Y, Chen Z (2025) Thermochemical Conversion of Sewage Sludge: Progress in Pyrolysis and Gasification. *Water* 17:1833. <https://doi.org/10.3390/w17121833>
36. Wasserman M, Moretti A, Goi D, Mainardis M (2025) Integrating renewable energy in sewage sludge treatment through greenhouse solar drying: A review. *Science of The Total Environment* 965:178634. <https://doi.org/10.1016/j.scitotenv.2025.178634>
37. Wang Z, Li X, Liu H, Mou J, Khan SJ, Lin CSK, Wang Q (2024) Evaluating energy balance and environmental footprint of sludge management in BRICS countries. *Water Research X* 25:100255. <https://doi.org/10.1016/j.wroa.2024.100255>
38. Werther J, Ogada T (1999) Sewage sludge combustion. *Progress in Energy and Combustion Science* 25:55–116. [https://doi.org/10.1016/S0360-1285\(98\)00020-3](https://doi.org/10.1016/S0360-1285(98)00020-3)
39. Qin S, He X, Li Z, Jia L, Qiao X, Chang X, Cheng P, Jin Y (2025) Co-combustion of sewage sludge and high ash coal: Thermal behavior, ash formation behavior, interaction mechanisms and economic analysis. *Energy* 323:135847. <https://doi.org/10.1016/j.energy.2025.135847>
40. Zhao C, Bai Y, Zhao W, Li Y, Song X, Wang J, Su W, Lv P, Yu G, Yao M (2025) Interaction between phosphorus and alkali/alkaline earth metals and their effect on ash transformation thermal kinetics during phosphorus-rich biomass and coal co-gasification. *Fuel* 394:135088. <https://doi.org/10.1016/j.fuel.2025.135088>
41. Shan Y, Zhou H, Sheng C (2024) Ash Formation and Associated Interactions during Co-Combustion of Wheat Straw and Sewage Sludge. *Energies* 17:1486. <https://doi.org/10.3390/en17061486>
42. Shehadeh D, Govin A, Grosseau P, Krou H, Bessette L, Ziegler G, Serclerat A (2024) Characterization of Ashes from Sewage Sludge–Limestone Incineration: Study of SSA Properties and Reactivity for SCM Use. *Construction Materials* 4:611–628. <https://doi.org/10.3390/constrmater4030033>
43. Franz M (2008) Phosphate fertilizer from sewage sludge ash (SSA). *Waste Management* 28:1809–1818. <https://doi.org/10.1016/j.wasman.2007.08.011>

44. Świerczek L, Cieřlik BM, Konieczka P (2021) Challenges and opportunities related to the use of sewage sludge ash in cement-based building materials – A review. *Journal of Cleaner Production* 287:125054. <https://doi.org/10.1016/j.jclepro.2020.125054>
45. Yu S, He P, Lü F, Zhang H (2025) Environmental impacts of sewage sludge incineration ash: Leaching characterization and scenario-based assessment. *Journal of Environmental Chemical Engineering* 13:117056. <https://doi.org/10.1016/j.jece.2025.117056>
46. Feldthus FB, Ottosen LM, Bertelsen IMG, Kirkelund GM (2025) Fluxing properties of sewage sludge ash in brick manufacturing: Effect of phosphorus extraction and brick clay composition. *Case Studies in Construction Materials* 23:e05387. <https://doi.org/10.1016/j.cscm.2025.e05387>

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