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Hydrometallurgical and pyrometallurgical valorization of blast furnace sludge from the Mălina settling pond (Galați, Romania)

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Abstract: In this study, blast furnace sludge from the Mălina settling pond, Galați, Romania, was investigated as an iron-bearing secondary resource whose reuse requires effective control of zinc and lead. The present study expands the previous conference contribution by extending the analytical dataset from 29 to 30 samples and integrating statistical, hydrometallurgical, and high-temperature treatment results. X-ray fluorescence analysis showed iron(III) oxide contents of 45.8834–86.1069 mass % (mean 65.7894 mass %), calcium oxide of 7.3885–25.6999 mass % (mean 16.3607 mass %), zinc oxide of 0.2899–1.5912 mass % (mean 0.6737 mass %), and lead oxide up to 0.3038 mass %. The high variability of lead oxide, sulfur trioxide, magnesium oxide, and arsenic(III) oxide confirmed localized enrichment within the pond. Apparent zinc removal from a high-zinc sample was 56.41% with sulfuric acid, 31.97% with carbon-dioxide-assisted leaching, and 2.24% with sodium hydroxide. Pretreatment at 400 °C increased subsequent carbon-dioxide-assisted removal to 58.40%, whereas calcination at 850 °C decreased subsequent acid-leaching performance to 28.28%. Coke addition increased the relative iron grade but did not ensure zinc depletion at intermediate temperatures. Strongly reduced or metallic products obtained at 1450–1600 °C contained very low zinc or zinc below the analytical detection limit. The results support selective feed management, targeted chemical treatment, and high-temperature reduction or melting for refractory high-zinc fractions, combined with rigorous capture and management of zinc- and lead-bearing secondary streams.

Keywords: blast furnace sludge, zinc removal, iron recovery, hydrometallurgy, pyrometallurgy

1. Introduction

Blast furnace sludge is a fine-grained residue generated during wet cleaning of blast furnace top gas. It contains particles derived from iron ore, coke, fluxes, and secondary compounds formed under ironmaking thermochemical conditions. Because these residues may contain substantial amounts of iron and carbon, they represent potentially valuable secondary raw materials. Their direct recycling is commonly restricted by zinc, lead, and other minor constituents that can adversely affect blast furnace operation and may also generate environmental concerns during long-term storage (Mansfeldt and Dohrmann, 2004; Das et al., 2007).

Zinc is particularly important because of its volatile and recirculating behaviour in ironmaking systems. In the high-temperature lower zones of a blast furnace, zinc-bearing compounds can be reduced and volatilized. In cooler regions, zinc vapours may subsequently reoxidize and condense, forming ZnO-rich deposits. Such internal recycling may disrupt burden descent, gas distribution, and the furnace thermal balance, and may promote the formation of accretions. Consequently, zinc input into the blast furnace must be controlled, and Zn-enriched sludge fractions generally require treatment before they can be returned to the ironmaking process (United States Steel Corporation, 1985; Besta et al., 2013; Trinkel et al., 2015).

The difficulty of zinc removal is governed not only by total Zn content but also by its chemical and mineralogical association. Literature on blast-furnace and steelmaking residues shows that relatively reactive Zn-bearing phases may be more readily dissolved or reduced, whereas Zn incorporated in Fe–

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Zn–O spinel-type structures can be considerably more resistant to conventional hydrometallurgical treatment (Van Herck et al., 2000; Kelebek et al., 2004; Stewart and Barron, 2020).

Several technological approaches have therefore been investigated to treat and valorize blast furnace sludge and related zinc-bearing residues. Physical separation and briquetting may be appropriate when a sufficiently low-zinc fraction can be isolated (Andersson et al., 2019). Hydrometallurgical routes may selectively dissolve Zn and Pb at moderate temperature, but they require reagent consumption, management of liquid effluents, and careful control of iron losses (Van Herck et al., 2000; Cantarino et al., 2012; Hamann et al., 2021). Pyrometallurgical routes exploit zinc volatility and may generate an iron-rich solid residue or a metallic product; however, successful implementation requires control of temperature, reducing conditions, off-gas cleaning, and secondary dust management (Trinkel et al., 2015; Hamann et al., 2021; Wei et al., 2023).

The Mălina settling pond near Galați represents an important Romanian case study because it contains a historical inventory of blast furnace sludge generated by the steel industry. A conference contribution presented at BMPC 2026 described the general technological problem and summarized selected characterization, leaching, and pilot-scale thermal-treatment results (Traistă et al., 2026). This PPMP article makes the relationship to that contribution explicit. The conference paper was based on 29 Mălina samples, whereas the present analytical dataset contains 30 samples from the same investigation. Previously reported leaching and Teliuc rotary-kiln data are identified as such. At the same time, this manuscript adds a complete 30-sample statistical treatment, detailed residue chemistry, additional thermal-pretreatment comparisons, detailed comparative thermochemical and cupola datasets, induction-melting and slag-fraction results, and an integrated interpretation of Zn/Pb behavior.

The objectives of this work are therefore: (i) to characterize the chemical variability of blast furnace sludge stored in the Mălina settling pond; (ii) to evaluate the efficiency and limitations of H_2SO_4, NaOH and CO_2-assisted leaching for zinc removal; (iii) to determine how thermal pretreatment and carbothermic conditions affect the iron-bearing fraction and residual Zn/Pb contents; (iv) to compare the behaviour of oxidic and metallic products generated at progressively higher treatment temperatures; and (v) to identify a technologically and environmentally appropriate route for producing a zinc-depleted iron-bearing or metallic product while ensuring controlled management of Zn- and Pb-bearing secondary streams.

2. Materials and methods

2.1. Sampling strategy and experimental design

This study investigated blast furnace sludge from the Mălina settling pond, Galați, Romania. The BMPC 2026 contribution used 29 samples from the pond. The analytical database was later extended to 30 samples by adding one more sample from the same investigation. Samples were collected from different sectors and from zones exhibiting visibly different consistency, colour and moisture in order to capture lateral and vertical heterogeneity. Excavation-controlled sampling was used because of the soft, plastic to semi-fluid consistency of parts of the deposit.

After collection, samples were dried, homogenized and deagglomerated. Representative subsamples were prepared for XRF characterization (Table 1). The experimental program combined: (i) complete chemical characterization and statistical assessment of the 30-sample dataset; (ii) comparative hydrometallurgical screening; (iii) thermal pretreatment prior to selected leaching routes; (iv) comparative thermochemical tests with different coke additions; (v) Zlăști cupola-type tests; and (vi) induction-furnace melting followed by slag-fraction characterization. The previously reported Teliuc rotary-kiln trials are used only as a pilot-scale benchmark (Fig. 1).

2.2. Provenance and status of the datasets

To avoid ambiguity regarding originality and data reuse, Table 2 identifies the provenance and role of each dataset. Data previously summarized in the BMPC 2026 conference paper are retained only where they provide necessary technological context and are explicitly cited as previously reported. The present article does not treat those data as entirely new.

Table 1. Average chemical composition of the Mălina blast furnace sludge based on the complete 30-sample dataset

Component	Mean content (wt.%)
Fe_2O_3	65.7894
CaO	16.3607
LOI	13.2529
MnO	1.2343
SiO_2	0.9374
ZnO	0.6737
SO_3	0.4629
MgO	0.2845
Al_2O_3	0.1870
Cl	0.1393
PbO	0.1190
As_2O_3	0.0225

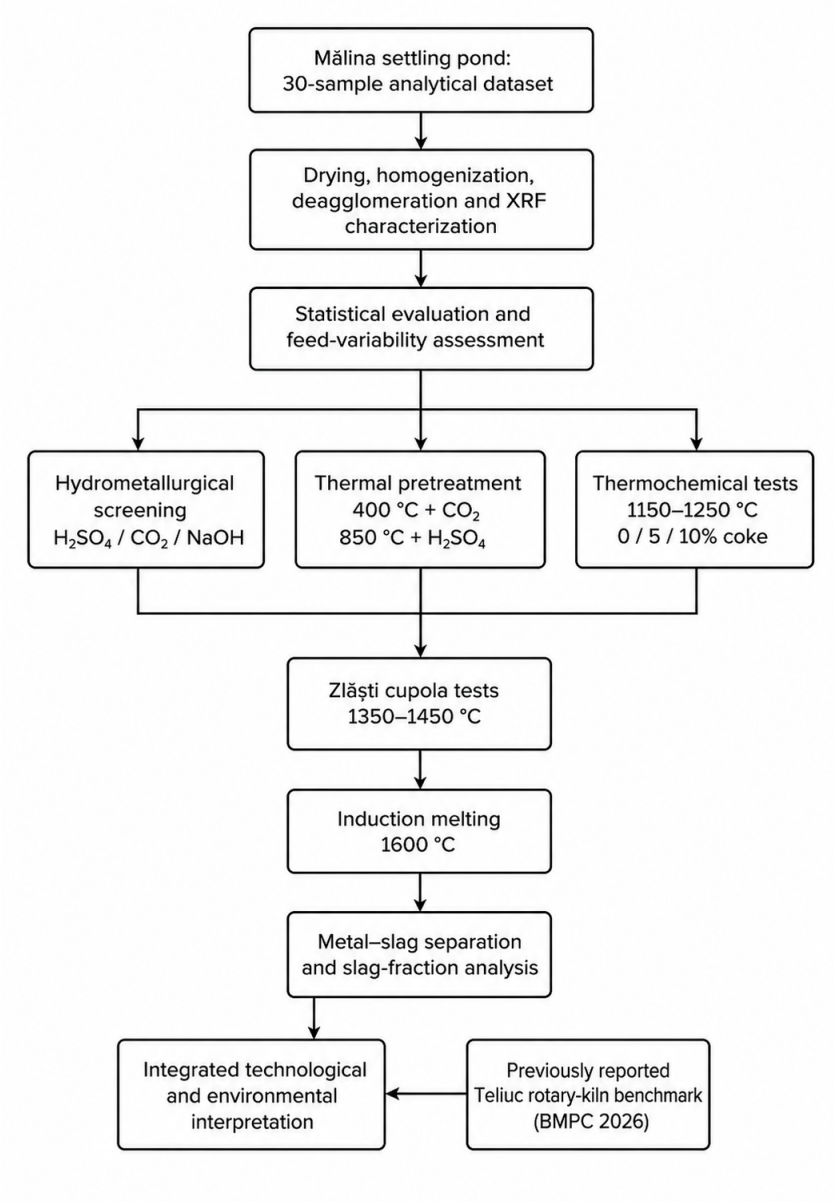

Fig. 1. Experimental workflow and relationship between the present datasets and the previously reported Teliuc benchmark

Table 2. Origin and role of the datasets used in the revised manuscript

Dataset	Material/treatment	Status	Role in present paper
Mălina chemical characterization	29-sample averages and ranges	Previously summarized at BMPC 2026	Baseline for comparison
Mălina chemical characterization	Complete 30-sample XRF dataset and expanded statistics	Extended in the present paper	Feed heterogeneity, skewness and outlier analysis
Leaching screening	Three H_2SO_4, CO_2 and NaOH series	Previously summarized at BMPC 2026	Reproducibility context
Leaching residue chemistry	Detailed XRF composition of representative residues	Expanded analysis in the present paper	Process selectivity and matrix response
Thermal pretreatment	400 °C + CO_2 and 850 °C + H_2SO_4	Not tabulated in the BMPC paper	Effect of pretreatment temperature
Câmpulung tests	1150–1250 °C; 0, 5 and 10 wt.% coke	Comparative dataset not included in BMPC tables	Effect of temperature and coke addition
Zlăşti tests	1350–1450 °C detailed product chemistry	Detailed dataset not tabulated at BMPC	High-temperature reduction and Zn partitioning
Induction melting	1600 °C metal and slag fractions	Detailed dataset not tabulated at BMPC	Metal recovery and slag partitioning
Teliuc rotary kiln	900–1100 °C pilot trials	Previously reported at BMPC 2026	Pilot-scale benchmark only

2.3. Chemical characterization and statistical treatment

Chemical composition was determined by X-ray fluorescence (XRF) and reported as major and minor oxides or, for metallic products, as elements. The principal components considered in the present paper were Fe_2O_3 or Fe, CaO, SiO_2, Al_2O_3, MgO, MnO/Mn, ZnO/Zn, PbO/Pb, SO_3, Cl and As_2O_3, together with carbon and loss on ignition where determined. For the Mălina sludge, Fe equivalent was calculated from Fe_2O_3 by stoichiometric conversion. For products reported as metallic materials, the analytical form originally determined was retained, and no oxide-to-metal conversion was imposed.

XRF analysis. Chemical composition was determined by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) using a Rigaku Supermini200 spectrometer (Rigaku Corporation, Tokyo, Japan) equipped with a Pd-target X-ray tube operated at 50 kV and 4 mA (200 W). The samples were dried, homogenized, finely ground, and prepared as pressed-powder specimens prior to analysis. The analytical procedure followed the Rigaku fundamental-parameter approach with matrix correction. Calibration performance and analytical accuracy were checked using certified reference materials, including NIST SRM 2710a (Montana I Soil), which contains certified mass fractions of 0.418 wt.% Zn, 0.552 wt.% Pb and 0.154 wt.% As. Each sample was measured in three analytical replicates, and the reported concentration represents the arithmetic mean of the replicate measurements. Analytical repeatability was evaluated as the relative standard deviation (RSD); the repeatability criterion was ≤2% for major components and ≤5% for Zn, Pb, and As. For this analytical procedure, the adopted method detection limits were 0.003 wt.% for Zn, 0.002 wt.% for Pb, and 0.004 wt.% for As (approximately 30, 20, and 40 mg kg^{-1}, respectively). Concentrations below these limits are reported as <LOD rather than as 0.0000. Where results are expressed as oxides, the corresponding elemental results were converted stoichiometrically. Descriptive statistics were calculated for the 30 Mălina samples, including mean, minimum, maximum, coefficient of variation (CV), median and skewness for the most heterogeneous components. Potential outliers were evaluated using the 1.5 × interquartile range (IQR) criterion. These parameters were used to assess whether the pond can be treated as a homogeneous feed or whether selective excavation and blending are required.

XRD screening. Representative Mălina sludge samples were also examined by powder X-ray diffraction (XRD) as a qualitative mineralogical screening step. The purpose was to identify the dominant crystalline phases and to assess whether discrete Zn-bearing phases could be resolved against the Fe-rich matrix. Fig. 2 presents the resulting diffraction pattern. The qualitative phase assignment

identified magnetite (MA), calcite (CA), graphite (GR), iron (IR), and wuestite (WU) as the principal identifiable crystalline constituents. Because the archived XRD record available for the present revision does not retain a complete set of instrument and scan-setting metadata, the XRD results are used qualitatively only, and no quantitative phase analysis is claimed.

2.4. Particle-size characterization and hydrometallurgical tests

The granulometric characterization available for the hydrometallurgical material is represented by sample 1C. The sample was predominantly fine-grained: 89.7 wt.% of the dry matter was below 250 μm, 82.7 wt.% below 125 μm, 74.1 wt.% below 63 μm, 69.6 wt.% below 45 μm, 45.3 wt.% below 16 μm and 24.7 wt.% below 2 μm. Table 3 gives the full cumulative distribution. These data are reported as the granulometric characterization used to describe the fineness of the sludge involved in the leaching program; the chemically selected high-Zn test sample is identified separately by its initial ZnO composition.

Table 3. Particle-size distribution of representative sample 1C

Particle-size fraction (μm)	Sample 1C (wt.% dry matter)
< 2000	92.3
< 1000	92.1
< 500	91.8
< 250	89.7
< 125	82.7
< 63	74.1
< 45	69.6
< 16	45.3
< 2	24.7

A high-zinc sludge sample containing 1.5912 wt.% ZnO and 67.4150 wt.% Fe_2O_3 was selected for comparative hydrometallurgical screening. Three treatment environments were investigated: sulfuric-acid leaching, CO_2-assisted leaching, and alkaline leaching with NaOH. Each route was investigated in three independent tests in the earlier experimental program. The previously reported Zn-removal results for the three independent tests were 54.8, 56.4, and 55.2% for H_2SO_4; 30.9, 32.0, and 34.0% for CO_2; and 2.0, 2.2, and 3.1% for NaOH (Traistă et al., 2026).

Leaching procedure. Acid leaching was performed using sulfuric acid (H_2SO_4). The leaching solution was prepared by diluting 96% H_2SO_4 with deionized water at an acid-to-water volumetric ratio of 1:10. A solid-to-liquid ratio of 1:3 (w/v) was used, corresponding to 1 g of dry sludge per 3 cm^3 of leaching solution. The experiments were conducted at 20 ± 1 °C for 2 h under continuous mechanical agitation at approximately 300 rpm (5 s^{-1}), sufficient to maintain the fine sludge particles in suspension and to minimize external mass-transfer limitations.

Alkaline leaching was performed using a 10 wt.% NaOH solution at a solid-to-liquid ratio of 1:3 (w/v). The tests were carried out at 20 °C for 2 h under continuous agitation at 300 rpm (5 s^{-1}). The treated suspension was subsequently subjected to the same solid–liquid separation, washing, drying, and XRF characterization procedure described for the acid-leaching tests.

CO_2-assisted leaching was carried out in a laboratory flotation machine equipped with a 3000 cm^3 cell. A solid-to-liquid ratio of 1:10 was used, the test temperature was maintained at 20 °C, and CO_2 was supplied at a gas flow rate of 10 L h^{-1} (2.78 cm^3 s^{-1}) for 2 h. The flotation cell provided continuous gas–slurry contact throughout the treatment, after which the solid residue was recovered and prepared for XRF analysis using the same separation and residue-preparation procedure.

At the end of the leaching period, the slurry was immediately separated by vacuum filtration through quantitative filter paper. The retained solid residue was washed with three successive portions of deionized water to remove residual soluble species and adhering leaching solution. The washed residue was then dried at 105 ± 2 °C to constant mass, cooled in a desiccator, homogenized, and

subsequently analyzed by XRF. The same solid–liquid separation and residue-preparation procedure was applied consistently to the comparative leaching tests.

Apparent zinc removal was calculated from the change in ZnO concentration in the solid residue according to Eq. (1):

$$R_{Zn,app}\ (\%) = [(C_0 - C_r)\ /\ C_0] \times 100 \quad (1)$$

where C_0 is the ZnO concentration in the untreated high-zinc sample, and C_r is the ZnO concentration in the treated solid residue. The term apparent removal is used because the calculation does not include the final solid mass or Zn concentration in the liquid phase and therefore does not represent a complete zinc mass balance.

Additional experiments examined whether thermal pretreatment modifies subsequent leaching behaviour. Acid leaching was compared for the original material and a material calcined at 850 °C. CO_2-assisted leaching was compared for the original material and a material thermally treated at 400 °C. These tests distinguished beneficial moderate activation from possible sintering or stabilization at higher temperatures.

2.5. Comparative thermochemical tests at Câmpulung

The Câmpulung dataset was used as a comparative thermochemical reference for the effects of temperature and coke addition on an iron-bearing sludge matrix. Treatments were performed at 1150 and 1250 °C and compared without added coke and with nominal additions of 5 and 10 wt.% coke. The resulting solids were characterized by XRF and interpreted as a comparative dataset separate from the 30-sample Mălina statistical population.

The thermochemical experiments at 1150 and 1250 °C were carried out in a continuously operated experimental rotary kiln having dimensions comparable to the drying drums used in small asphalt-mixing plants. The cylindrical working section was approximately 6.0 m long and 1.2 m in internal diameter. The kiln was operated at approximately 10–12 rpm (0.167–0.200 s^{-1}), with an inclination of approximately 3%, and the dry sludge feed rate was maintained at 200 kg h^{-1} (0.0556 kg s^{-1}).

The 5 and 10 wt.% coke additions were defined relative to the dry mass of the sludge feed. Accordingly, at a sludge feed rate of 200 kg h^{-1} (0.0556 kg s^{-1}), the nominal coke addition rates were 10 kg h^{-1} (0.00278 kg s^{-1}) for the 5 wt.% condition and 20 kg h^{-1} (0.00556 kg s^{-1}) for the 10 wt.% condition. The corresponding total material feed rates were approximately 210 and 220 kg h^{-1} (0.0583 and 0.0611 kg s^{-1}), respectively.

Coke was added primarily to establish and maintain a reducing environment within the moving material bed, thereby promoting carbothermic reduction of ZnO and Zn–Fe–O compounds and facilitating the conversion of zinc to volatile metallic Zn. In addition, the carbonaceous reductant promotes the generation of CO through the Boudouard reaction, lowers the local oxygen potential, contributes to the partial reduction of iron oxides, favours enrichment and/or metallization of the iron-bearing fraction, and limits reoxidation of reduced species within the solid bed. Coke can also contribute to the thermal balance through oxidation of carbon and CO in the freeboard region and helps maintain reducing conditions despite local variations in gas composition.

For the adopted kiln geometry and operating conditions, the mean residence time of the solids was estimated using the Sullivan-type relationship (Eq. 2):

$$t = 0.19\ L/(N \cdot D \cdot S) \quad (2)$$

where t is the mean residence time in minutes, L is the effective kiln length, D is the internal diameter, N is the rotational speed, and S is the kiln slope expressed as m/m. For L = 6.0 m, D = 1.2 m, S = 0.03 and N = 10–12 rpm (0.167–0.200 s^{-1}), the calculated mean residence time ranges from approximately 3.17 min (190 s) at 10 rpm (0.167 s^{-1}) to 2.64 min (158 s) at 12 rpm (0.200 s^{-1}), with a representative value of approximately 2.88 min (173 s) at 11 rpm (0.183 s^{-1}).

At the nominal sludge feed rate of 200 kg h^{-1} (0.0556 kg s^{-1}), this residence time corresponds to an average sludge hold-up of approximately 9.6 kg inside the kiln at 11 rpm (0.183 s^{-1}). When the coke addition is included, the corresponding mean total bed hold-up is approximately 10.1 kg for the 5 wt.% coke condition and 10.6 kg for the 10 wt.% coke condition.

Reducing conditions were generated within the material bed by the added coke rather than by an externally supplied inert atmosphere. After discharge, the thermally treated products were allowed to

cool under conditions limiting excessive contact with air in order to minimize reoxidation before homogenization and XRF analysis. Each temperature–coke combination was treated as a separate continuous experimental condition, and representative product samples were collected after stable operating conditions had been established. Because the archived records do not document independent process replication of the Câmpulung rotary-kiln runs, no process-level statistical replication is claimed; analytical replication and uncertainty refer to the XRF measurements described in Section 2.3.

2.6. Zlăști cupola tests

Cupola-type tests at Zlăști were used to assess the behaviour of sludge-derived iron-bearing products at 1350 and 1450 °C. At 1350 °C, treatments without added coke and with 5 and 10 wt.% coke were compared. At 1450 °C, the charge contained 8 wt.% coke relative to the dry sludge mass, and reduced iron together with a sponge-like iron-rich product was obtained. The analytical form reported for each product was retained: metallic products are expressed as elemental Fe/Mn where appropriate, whereas oxidic products are expressed as Fe_2O_3, MnO and other oxides.

The 8 wt.% coke addition at 1450 °C was used to establish sufficiently reducing conditions for decomposition and reduction of refractory Zn-bearing compounds, promote Zn volatilization, and enhance reduction and metallization of the iron-bearing fraction. This dosage was intermediate between the 5 and 10 wt.% coke conditions examined at 1350 °C.

The high-temperature experiments performed at Zlăști were carried out in an experimental cupola furnace operated with discrete 100 kg sludge-based charges. The furnace operated according to the conventional cupola principle, with coke serving as both fuel and carbonaceous reductant. Combustion air was supplied through the tuyeres, producing an oxidizing combustion zone in their immediate vicinity and a CO-rich reducing zone above the coke bed. No externally supplied inert or reducing gas was used; the reducing atmosphere was generated in situ by the interaction of coke with the combustion gases.

For the experiments conducted at 1350 °C, the 100 kg charges were tested without additional coke and with 5 and 10 wt.% coke, corresponding to approximately 5 and 10 kg coke per 100 kg of dry sludge, respectively. For the 1450 °C experiment, 8 wt.% coke was added, corresponding to approximately 8 kg coke per 100 kg of dry sludge. Coke addition was used to lower the local oxygen potential, promote CO formation, support carbothermic reduction of Zn-bearing phases, favour zinc volatilization, and enhance partial reduction and metallization of the iron-bearing fraction.

Before each experimental run, the coke bed was brought to stable operating conditions, and the charge was preheated in the upper furnace zone. After establishing the target thermal regime, the material was maintained under the corresponding high-temperature reducing conditions for approximately 30 min (1800 s) before discharging the product. This holding period was selected to allow reduction, zinc volatilization, and metal/slag separation to proceed under a stable thermal regime.

At the end of each test, the metallic/iron-rich product and slag were discharged separately. The products were allowed to cool naturally in air in refractory or steel receiving containers to ambient temperature, after which they were collected, homogenized, and prepared for XRF analysis. Rapid water quenching was avoided for the analytical samples in order to prevent additional hydration, fragmentation, and alteration of the solid phases prior to chemical characterization. The cooling rate was not actively controlled or recorded.

Each temperature/coke condition was treated as a separate process-scale experimental condition. Representative product samples were collected after the thermal regime had stabilized. Because the available records do not document statistical replication of the thermal runs, no process-level replication is claimed; analytical replication of the XRF measurements is reported separately.

2.7. Induction-furnace melting and slag separation

Induction-furnace melting was performed at 1600 °C to evaluate whether a pig-iron-type metallic product could be obtained. The resulting metallic product was characterized by Fe and C contents and residual oxide constituents. The associated slag was separated into magnetic and non-magnetic fractions and characterized by XRF. The available dataset does not specify a separately quantified external coke percentage for the 1600 °C test; therefore, this paper assigns no unverified coke dosage.

The final high-temperature melting experiment was carried out in a laboratory-scale induction furnace using a relatively small graphite crucible fitted with a graphite lid. The crucible had an external diameter of approximately 80 mm and a height of 100 mm, with an internal diameter of approximately 60 mm. The graphite lid remained in place during heating and holding to limit direct contact between the charge and atmospheric oxygen.

A 0.5 kg charge of dried and homogenized material was introduced into the graphite crucible, leaving sufficient free volume for slag formation and metal–slag separation. The furnace was heated progressively to 1600 °C. After complete melting and establishment of a stable metal–slag system, the material was maintained at the target temperature for approximately 15 min (900 s) to allow reduction reactions, zinc volatilization, and gravity-assisted separation between the denser Fe–C metallic phase and the less dense oxidic slag.

No external inert or reducing gas was supplied. Reducing conditions developed locally inside the covered graphite crucible as a consequence of the direct contact of the charge with graphite and the generation of CO at high temperature. The graphite crucible and lid therefore performed a dual function: containment of the molten charge and contribution to the low-oxygen-potential environment required for carbothermic reduction. These conditions favour reduction of ZnO and Zn–Fe–O compounds, volatilization of Zn, partial to extensive reduction of iron oxides and carbon transfer to the metallic phase.

At the end of the holding period, induction power was switched off, and the covered crucible was allowed to cool naturally under the graphite lid, thereby limiting rapid reoxidation of the metallic product. After cooling to room temperature, the crucible contents were mechanically separated into the metallic Fe–C product and the associated slag. Representative samples of both phases were subsequently prepared for chemical analysis. The cooling rate was not actively controlled or recorded.

The solidified slag was crushed and homogenized before magnetic separation. The slag was reduced to a particle size below approximately 1 mm and subjected to dry low-intensity magnetic separation, using a magnetic field of approximately 0.2 T. The procedure produced a magnetic iron-bearing fraction and a non-magnetic fraction, both of which were analyzed separately by XRF. The purpose of this stage was to evaluate the potential recovery of residual iron-bearing particles from the slag and the preferential distribution of Zn and Pb between the magnetic and non-magnetic fractions.

The induction-melting experiment was treated as a process-scale experimental test. The resulting metallic product, magnetic slag fraction, and non-magnetic slag fraction were each homogenized and characterized separately. Because the available records do not document statistical replication of the furnace run, no process-level replication is claimed; analytical replication of the XRF measurements is reported separately.

2.8. Previously reported Teliuc rotary-kiln benchmark

The Teliuc rotary-kiln dataset was previously reported in the BMPC 2026 conference contribution and is retained here solely as a pilot-scale technological benchmark (Traistă et al., 2026). The pilot installation comprised a rotary kiln approximately 8 m long and 0.8 m in internal diameter, with adjustable rotational speed of 0.5–2 rpm (0.0083–0.0333 s^{-1}) and controlled air supply. Prior to treatment, the sludge was mechanically homogenized, partially dried to below approximately 10% moisture, and freed of oversized agglomerates. The trials were performed over approximately 900–1200 °C, with strong zinc volatilization reported in the 1000–1100 °C range. Residence time was approximately 30–60 min (1800–3600 s), the excess-air coefficient was 1.05–1.15, and kiln inclination was 2–3%. Zinc-rich dust was collected downstream using cyclones and bag filters.

The BMPC paper describes the carbonaceous matter naturally present in the sludge as an internal reducing agent. The available source does not report a fixed external coke-to-feed ratio for the Teliuc pilot trials; therefore, we do not introduce one retrospectively.

3. Results and discussion

3.1. Chemical variability of the Mălina blast furnace sludge

The 30-sample chemical dataset demonstrates that the Mălina material is strongly iron-bearing but chemically heterogeneous. Fe_2O_3 ranged from 45.8834 to 86.1069 wt.%, with a mean of 65.7894 wt.%. Expressed as stoichiometric Fe equivalent, the mean corresponds to approximately 46.02 wt.% Fe. CaO

was the second major oxide, ranging from 7.3885 to 25.6999 wt.% with a mean of 16.3607 wt.%. This variation confirms that the pond should not be treated as a chemically uniform feed.

The main restrictions on direct metallurgical recycling involve Zn and Pb. ZnO ranged from 0.2899 to 1.5912 wt.% (mean 0.6737 wt.%), whereas PbO ranged from values reported as analytical zero/below detection to 0.3038 wt.% (mean 0.1190 wt.%). The ZnO coefficient of variation was 44.64%, considerably higher than that of Fe_2O_3, indicating substantial spatial variation of the zinc content.

Even greater coefficients of variation were obtained for PbO (82.50%), SO_3 (83.11%), MgO (70.06%) and As_2O_3 (204.85%). The distributions were not symmetric. PbO had a median of 0.0799 wt.% and skewness +0.71. SO_3 had a median of 0.3112 wt.% and skewness +2.66; five upper outliers were identified by the 1.5 × IQR criterion (0.6564, 0.7284, 1.2906, 1.4020 and 1.8719 wt.%). MgO had a median of 0.2310 wt.% and skewness +2.54, with one upper outlier at 1.1009 wt.%. ZnO had a median of 0.5732 wt.% and skewness +1.19, with the 1.5912 wt.% sample identified as an upper outlier. As_2O_3 had a median of 0 and was numerically reported above zero in seven of the 30 samples, reaching a maximum of 0.1535 wt.%, indicating strongly localized occurrence.

These statistical results strengthen the technological case for selective excavation, feed characterization and blending. Elevated values are associated with localized enrichments rather than a simple uniform shift in composition across the pond. Consequently, the efficiency of any hydrometallurgical or pyrometallurgical process will depend partly on how the sludge is excavated, homogenized and classified before treatment.

Table 4. Statistical parameters of selected components in the Mălina blast furnace sludge (n = 30)

Component	Mean (wt.%)	Minimum (wt.%)	Maximum (wt.%)	CV (%)	Technological Significance
Fe_2O_3	65.7894	45.8834	86.1069	13.99	dominant iron-bearing component
CaO	16.3607	7.3885	25.6999	21.89	acid consumption / slag basicity
LOI	13.2529	0.1652	26.3282	44.78	carbonaceous/hydrated contribution
MnO	1.2343	0.8547	1.6091	14.19	associated with iron-bearing material
SiO_2	0.9374	0.5150	1.6967	30.07	minor silicate dilution
ZnO	0.6737	0.2899	1.5912	44.64	main technological restriction
PbO	0.1190	<0.0022*	0.3038	82.50	volatile and highly variable
SO_3	0.4629	0.2309	1.8719	83.11	strongly heterogeneous sulfate-bearing component
MgO	0.2845	0.0720	1.1009	70.06	localized magnesian enrichment
Al_2O_3	0.1870	0.0983	0.3976	38.15	minor aluminosilicate contribution
Cl	0.1393	0.0377	0.2561	36.04	soluble salts/process-related component
As_2O_3	0.0225	<0.0053*	0.1535	204.85	strongly localized trace component

* The elemental analytical detection limits adopted in Section 2.3 correspond approximately to 0.0022 wt.% PbO and 0.0053 wt.% As_2O_3. Historical analytical zeros were retained as zero for calculation of descriptive statistics, but are reported qualitatively as below the corresponding oxide-equivalent detection limit.

3.2. XRD characterization and mineralogical implications for zinc removal

X-ray diffraction analysis of the input Mălina sludge sample revealed a crystalline assemblage dominated by Fe-bearing and Ca-bearing phases (Fig. 2). The principal identifiable phases were magnetite (MA), calcite (CA), graphite (GR), iron (IR) and wuestite (WU). The occurrence of magnetite, iron and wuestite is consistent with the strongly Fe-rich character of the sludge and its origin from ironmaking gas-cleaning residues. In contrast, graphite reflects the carbonaceous fraction derived

mainly from coke. Calcite represents an important Ca-bearing constituent and is consistent with the comparatively high CaO contents determined by XRF.

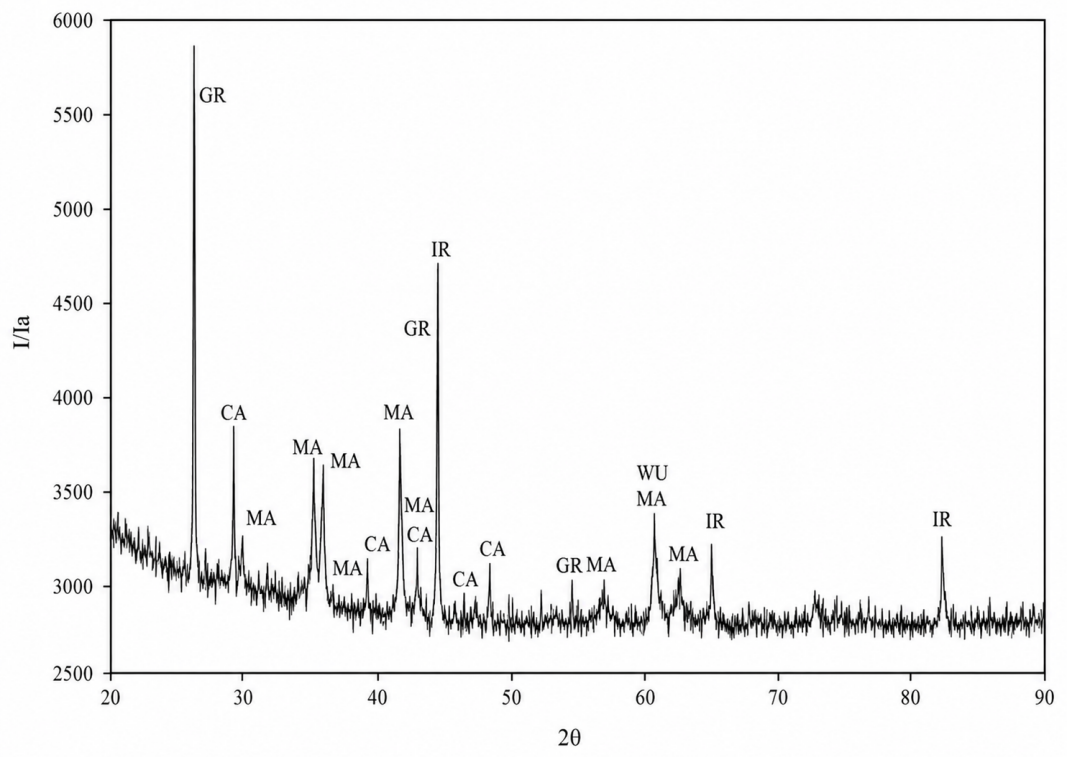

Fig. 2. X-ray diffraction pattern of the input sample (MA – magnetite, CA – calcite, GR – graphite, IR – iron, WU – wuestite)

Despite the ZnO concentrations determined by XRF, no discrete Zn-bearing crystalline phase was unequivocally identified in the XRD pattern. In particular, neither zincite nor a distinct zinc ferrite/franklinite reflection could be resolved. This result does not imply that Zn-bearing mineralogical associations are absent. The total Zn concentration is comparatively low relative to the dominant Fe-bearing matrix, and Zn may occur in finely dispersed, poorly crystalline or structurally incorporated forms.

A further difficulty concerns the possible occurrence of a zinc ferrite/franklinite-type spinel. Magnetite and franklinite have closely related spinel structures and show substantial diffraction-peak overlap, particularly in the approximately 30–36°, 43° and 57–63° 2θ regions. Consequently, a minor Zn-bearing spinel component may be masked by the considerably more abundant magnetite reflections (Van Herck et al., 2000; Kelebek et al., 2004; Stewart and Barron, 2020).

Although XRD did not directly identify franklinite, the sludge's chemical behavior supports its possible occurrence. H_2SO_4 leaching removed only part of the Zn, whereas CO_2-assisted and NaOH leaching were less effective, and calcination at 850 °C decreased the subsequent acid-leaching response. These observations indicate a refractory Zn fraction with limited chemical accessibility and are consistent with Zn–Fe–O spinel-type associations reported for blast-furnace and steelmaking residues (Van Herck et al., 2000; Kelebek et al., 2004; Stewart and Barron, 2020).

The high-temperature results provide complementary evidence. At 1350 °C, increasing coke addition did not ensure Zn depletion from the retained oxidic product. In contrast, treatment at 1450 °C with 8 wt.% coke produced a strongly reduced Fe-rich product in which Zn was below the adopted analytical detection limit. This behaviour is consistent with decomposition and carbothermic reduction of a refractory Zn–Fe–O fraction at sufficiently high temperature and low oxygen potential.

Taken together, the XRD, XRF, leaching and high-temperature results support the presence of a refractory Zn-bearing fraction, most plausibly including zinc ferrite/franklinite-type associations, while avoiding the unsupported conclusion that franklinite was directly identified in the diffraction pattern (Mansfeldt and Dohrmann, 2004; Xue et al., 2022).

3.3. Hydrometallurgical screening of the high-zinc sample

The high-zinc sample used for comparative leaching contained 1.5912 wt.% ZnO and 67.4150 wt.% Fe_2O_3. Acid leaching was the most effective treatment under the investigated conditions. ZnO decreased to 0.6936 wt.%, corresponding to 56.41% apparent zinc removal. At the same time, Fe_2O_3 increased to 95.2998 wt.%, reflecting relative enrichment of the iron-bearing residue after removal of other components rather than a directly mass-balanced iron recovery. CaO decreased from 14.9346 to 1.0343 wt.%, demonstrating substantial attack on reactive Ca-bearing constituents.

CO_2-assisted leaching produced an intermediate response: ZnO decreased to 1.0825 wt.%, corresponding to 31.97% apparent removal, while CaO remained high. NaOH leaching was ineffective under the tested conditions, with ZnO decreasing only to 1.5555 wt.% (2.24% apparent removal). The earlier experimental program included three independent tests for each route; the corresponding removal values were 54.8–56.4% for H_2SO_4, 30.9–34.0% for CO_2, and 2.0–3.1% for NaOH (Traistă et al., 2026).

These results show that sulfuric-acid leaching can produce an iron-enriched solid residue. Still, residual Zn remains technologically relevant, and the strong dissolution of Ca-bearing material implies significant reagent consumption and an aqueous secondary stream requiring treatment. Hydrometallurgy should therefore be considered a selective or complementary treatment rather than a complete solution for all high-zinc sludge fractions.

Table 5. Preliminary leaching results for the high-zinc Mălina sludge sample

Component	Original	H_2SO_4 leaching	CO_2 leaching	NaOH leaching
MgO	0.0720	0.0000	0.1514	0.2760
CaO	14.9346	1.0343	15.5055	17.4388
Fe_2O_3	67.4150	95.2998	66.6970	63.8999
ZnO	1.5912	0.6936	1.0825	1.5555
PbO	0.1353	<0.0022	0.2476	0.5499
LOI	12.7416	0.0000	13.5117	11.8073
Apparent Zn removal [%]	–	56.41	31.97	2.24

3.4. Effect of thermal pretreatment on leaching response

Thermal pretreatment produced opposite effects depending on temperature and the subsequent leaching route. Direct H_2SO_4 leaching gave 56.41% apparent Zn removal, whereas after calcination at 850 °C followed by acid leaching, the solid residue contained 1.1412 wt.% ZnO. Using the same initial concentration of 1.5912 wt.% ZnO, the apparent removal after pretreatment was 28.28%.

The lower acid-leaching response after 850 °C calcination suggests that the higher-temperature pretreatment did not activate the zinc-bearing material under the investigated conditions. Possible explanations include sintering, reduced porosity, recrystallization, or stabilization of less acid-accessible Fe–Zn–O associations; without direct mineralogical or porosity measurements, these mechanisms are presented as interpretations rather than demonstrated transformations.

A different response was observed after 400 °C pretreatment. Subsequent CO_2-assisted leaching produced a residue containing 0.6619 wt.% ZnO, corresponding to 58.40% apparent Zn removal compared with 31.97% for direct CO_2-assisted leaching. Moderate heating may remove water and volatile components and modify access to reactive surfaces without the stronger structural changes associated with 850 °C treatment. Overall, the data show that thermal pretreatment is not uniformly beneficial and must be selected based on the intended downstream treatment.\

3.5. Comparative thermochemical tests at 1150–1250 °C

The comparative Câmpulung dataset was used to examine the combined effects of temperature and coke addition. The initial material contained 68.6527 wt.% Fe_2O_3, 19.2760 wt.% CaO and 0.5745 wt.% ZnO. At 1150 °C without coke, Fe_2O_3 decreased to 63.8834 wt.%; addition of 5 and 10 wt.% coke

increased the reported Fe_2O_3 concentration to 71.3500 and 72.3569 wt.%, respectively. At 1250 °C, the products contained 70.5404 wt.% Fe_2O_3 without coke, 71.1005 wt.% with 5 wt.% coke and 72.2650 wt.% with 10 wt.% coke.

The relative Fe_2O_3 enrichment in coke-containing solids should not be interpreted directly as equivalent absolute iron recovery because no complete solid mass balance is available. More importantly, coke addition did not decrease ZnO in the retained solids. ZnO remained between 0.5398 and 0.6613 wt.% and was higher than the initial 0.5745 wt.% in all coke-containing products. This apparent increase may reflect relative concentration after mass loss, persistence of refractory Zn-bearing material, or volatilization followed by redeposition. Without off-gas/dust analysis, these mechanisms cannot be distinguished.

Table 6. Effect of thermal pretreatment on subsequent zinc leaching

Leaching Route	Pretreatment	ZnO in Direct-leach Residue (wt.%)	ZnO after Pretreatment + leaching (wt.%)	Apparent Removal without Pretreatment (%)	Apparent Removal after Pretreatment (%)	Interpretation
H_2SO_4 leaching	850 °C calcination	0.6936	1.1412	56.41	28.28	less favourable after 850 °C
CO_2 leaching	400 °C treatment	1.0825	0.6619	31.97	58.40	moderate pretreatment improves response

Table 7. Comparative thermochemical tests on Câmpulung iron-bearing sludge

Component	Initial	1150 °C	1150 °C + 5% coke	1150 °C + 10% coke	1250 °C	1250 °C + 5% coke	1250 °C + 10% coke
Fe_2O_3	68.6527	63.8834	71.3500	72.3569	70.5404	71.1005	72.2650
Fe equiv.	48.0569	44.7184	49.9450	50.6498	49.3783	49.7704	50.5855
CaO	19.2760	21.2796	19.2022	19.8171	23.1107	20.3088	18.8374
SiO_2	5.3000	8.1020	3.6178	2.6493	1.4171	2.9202	3.6519
ZnO	0.5745	0.5398	0.6552	0.6388	0.5952	0.6613	0.6559
PbO	0.1001	0.2148	0.3328	0.1472	0.2730	0.3134	0.3359

3.6. Zlăşti cupola tests: temperature effect and zinc partitioning

At 1350 °C, the products remained predominantly oxidic. Addition of coke increased Fe_2O_3 from 73.0205 wt.% without coke to 83.2344 wt.% with 5 wt.% coke and 85.1431 wt.% with 10 wt.% coke. At the same time, ZnO increased from 0.4077 to 0.7984 wt.% in the 10 wt.% coke product, and PbO reached 0.7408 wt.%. Thus, coke addition at 1350 °C increased the relative iron grade but did not remove Zn and Pb from the retained solid.

At 1450 °C, using an 8 wt.% coke addition, a distinctly different product regime was obtained. The reduced iron product contained 93.3679 wt.% Fe and 3.6854 wt.% C, while Zn was below the adopted analytical detection limit (<0.003 wt.% Zn). The sponge-like material contained 93.7371 wt.% Fe_2O_3 on an oxidic analytical basis and 0.0997 wt.% ZnO. Compared with the 1350 °C experiments, the combination of higher temperature and an 8 wt.% coke addition produced substantially stronger reduction and more effective rejection of Zn from the Fe-rich metallic phase. Because the reduced iron and sponge-like product are reported on different analytical bases, their Fe values are not directly comparable.

The comparison indicates that formation of a strongly reduced or metallic phase is more decisive for rejecting Zn from the recovered Fe-rich product than coke addition alone at 1350 °C. However, Zn rejection from the metal does not establish overall zinc removal from the system; volatilized zinc must be captured in the off-gas/dust stream.

Values are retained in the analytical form originally reported for each product. The adopted Zn detection limit is 0.003 wt.%.

Table 8. Results of the Zlăşti cupola tests

Component	1350 °C	1350 °C + 5% coke	1350 °C + 10% coke	1450 °C + 8 wt.% coke reduced iron	1450 °C + 8 wt.% coke sponge material
MgO	0.2577	0.0000	0.1964	–	0.0000
Al_2O_3	1.2537	0.3461	0.9228	0.1410	0.0873
SiO_2	8.0441	5.7733	2.0233	0.3928	1.2776
CaO	12.5991	6.3969	5.3554	0.0000	0.3920
MnO/Mn	1.4201 MnO	1.4067 MnO	1.1749 MnO	0.4769 Mn	0.2672 MnO
Fe_2O_3/Fe	73.0205 Fe_2O_3	83.2344 Fe_2O_3	85.1431 Fe_2O_3	93.3679 Fe	93.7371 Fe_2O_3
ZnO/Zn	0.4077 ZnO	0.4627 ZnO	0.7984 ZnO	<0.003 wt.% Zn	0.0997 ZnO
PbO/Pb	0.1229 PbO	<0.0022 PbO	0.7408 PbO	0.2044 Pb	0.1661 PbO
C	–	–	–	3.6854	–

3.7. Induction-furnace melting and slag separation

The induction-furnace experiment at 1600 °C produced a metallic Fe–C product containing 95.5262 wt.% Fe and 3.6854 wt.% C. The reported concentrations of residual oxide constituents were comparatively low: 0.4188 wt.% Al_2O_3, 1.2885 wt.% SiO_2, 0.7717 wt.% CaO and 0.8156 wt.% MnO. MgO was below the reported detection limit. Zn was below the adopted analytical detection limit (<0.003 wt.% Zn) in the metallic product.

The result demonstrates separation of Zn from the metallic phase, not disappearance of zinc from the overall system. At these temperatures, zinc can be reduced and volatilized before reoxidizing or condensing in cooler parts of the gas path. Industrial validation therefore requires complete Zn and Pb mass balances including feed, metal, slag, dust and deposits (Stewart and Barron, 2020; Wei et al., 2023).

The slag-separation results provide additional information on partitioning. The magnetic slag fraction contained 0.2813 wt.% ZnO and 0.0578 wt.% PbO, whereas the non-magnetic fraction contained 0.9260 wt.% ZnO and 0.3225 wt.% PbO. This indicates preferential concentration of Zn and Pb in the non-magnetic fraction relative to the magnetic fraction. Crushing and physical separation of slag may therefore form part of an integrated flowsheet, provided the enriched non-magnetic fraction is managed as a controlled secondary stream.

Metallic and oxide values are retained in the analytical form originally reported. The adopted Zn detection limit is 0.003 wt.%.

Table 9. Induction-furnace pig iron and magnetic separation of the resulting slag

Component	Pig iron at 1600 °C	Magnetic slag fraction	Non-magnetic slag fraction
MgO	b.d.l.	0.4895	0.4279
Al_2O_3	0.4188	1.5973	2.5501
SiO_2	1.2885	9.0730	13.6901
CaO	0.7717	37.8125	54.7018
MnO	0.8156	3.6353	5.5383
Fe/Fe_2O_3	95.5262 Fe	11.5785 Fe_2O_3	17.8132 Fe_2O_3
ZnO/Zn	<0.003 wt.% Zn	0.2813 ZnO	0.9260 ZnO
PbO	0.0912	0.0578	0.3225
C	3.6854	–	–

3.8. Previously reported Teliuc rotary-kiln benchmark

The Teliuc pilot-scale data are included only to provide an intermediate technological benchmark between low-temperature chemical treatment and high-temperature melting. The previously reported trials gave Zn removals of 79.9, 82.2 and 76.2% over temperature ranges of 900–1000, 950–1050 and 1000–1100 °C, respectively (Traistă et al., 2026). These values show that a rotary kiln can achieve substantial

Zn volatilization while retaining an iron-rich solid residue. However, performance depends on feed uniformity, residence time, gas supply, and control of the reducing atmosphere.

The technological objective of rotary-kiln treatment differs from induction melting. The kiln route aims to volatilize zinc while retaining a solid iron-bearing residue, whereas induction melting aims to form a metallic phase and a separate slag. The two routes therefore represent different process intensities and product targets.

Table 10. Previously reported Teliuc pilot-scale rotary-kiln benchmark (Traistă et al., 2026)

Test	Temperature Range (°C)	Fe Content (%)	Zn Content (%)	Zn Removal (%)
Teliuc test 1	900–1000	50.85	4.33	79.9
Teliuc test 2	950–1050	41.93	3.83	82.2
Teliuc test 3	1000–1100	52.88	5.14	76.2

3.9. Integrated technological interpretation

The experimental results show that treatment strategy cannot be selected solely from total Fe or total Zn. Feed heterogeneity, Ca content, chemical accessibility of Zn and the degree of thermal reduction all influence process performance. The first requirement is therefore appropriate feed management. The 30-sample dataset shows that selective excavation, characterization, and blending can reduce fluctuations in Fe, Ca, Zn, Pb, SO_3, and As before treatment.

For chemically accessible Zn-bearing fractions, hydrometallurgical treatment can partially dezinc. H_2SO_4 gave the highest apparent Zn removal in the direct screening tests but strongly attacked the Ca-bearing matrix. CO_2-assisted treatment was milder and improved substantially after 400 °C pretreatment. NaOH was ineffective under the tested conditions. The contrast between 400 and 850 °C pretreatment demonstrates that calcination temperature must be coupled to the downstream route.

At higher temperature, coke addition increased the relative Fe grade of retained solids but did not consistently decrease Zn. A more pronounced change occurred when strongly reduced or metallic phases formed at 1450–1600 °C, where Zn was very low or below detection in the Fe-rich product. This transition is a key technological threshold, but it must not be confused with complete zinc removal from the process. Complete validation requires accounting for dust, slag, leachate, and condensed deposits.

A conceptual treatment sequence supported by the present results is: selective excavation and blending → drying and homogenization → chemical characterization and feed classification → optional mild hydrometallurgical treatment for suitable fractions → high-temperature reduction or melting for refractory/high-Zn fractions → metal–slag separation → recovery of residual iron-bearing slag fractions → efficient off-gas cleaning and Zn/Pb-rich dust collection. Hydrometallurgical and pyrometallurgical operations should therefore be regarded as potentially complementary rather than mutually exclusive.

3.10. Environmental significance and control of secondary streams

The environmental significance of valorizing the Mălina sludge is associated both with iron recovery and with reduction of the long-term burden created by storage of fine metallurgical residue containing Zn, Pb, Cl, sulfate-bearing constituents and locally elevated As. A sustainable process must therefore consider not only the quality of the recovered iron product but also the quantity and composition of all secondary streams.

Hydrometallurgical processing generates an aqueous secondary stream. During acid leaching, CaO in the solid decreased from 14.9346 to 1.0343 wt.%, demonstrating extensive dissolution of the Ca-bearing matrix. This implies substantial acid consumption and a leachate that may contain Ca alongside Zn, Pb, and other soluble constituents. The apparent Zn removal must therefore be assessed alongside reagent demand, neutralization requirements, and management of the resulting treatment sludge.

Pyrometallurgical processing produces a different secondary-stream challenge. Zn below detection in the metallic product indicates transfer elsewhere in the system, most plausibly through volatilization followed by oxidation/condensation. If efficiently captured, the Zn-rich dust becomes a concentrated secondary stream that can be managed or further treated. If capture is inefficient, the process can merely

relocate contamination. Gas-cleaning efficiency is therefore a core process criterion rather than an auxiliary environmental measure (Trinkel et al., 2015; Stewart and Barron, 2020).

From a circular-economy perspective, the preferred route should maximize iron recovery while concentrating Zn and Pb into the smallest practical and controllable secondary stream. Valorization may therefore provide a dual benefit: recovering a secondary iron resource and reducing the quantity of fine metallurgical sludge requiring long-term storage. Demonstrating this benefit at industrial scale requires complete Fe–Zn–Pb mass balances and environmental characterization of leachates, slags, dusts, and deposits.

4. Conclusions

Blast furnace sludge from the Mălina settling pond is a heterogeneous but strongly iron-bearing secondary material. Chemical characterization of 30 samples showed Fe_2O_3 concentrations between 45.8834 and 86.1069 wt.% (mean 65.7894 wt.%), whereas ZnO reached 1.5912 wt.% and PbO reached 0.3038 wt.%. The high CV values and positively skewed distributions of several minor components, particularly SO_3, MgO, ZnO and As_2O_3, demonstrate that the pond should not be treated as a homogeneous feed.

This paper explicitly distinguishes the earlier 29-sample BMPC 2026 dataset and previously reported leaching/Teliuc results from the extended 30-sample statistical analysis and the more detailed thermal, cupola, induction-melting and slag-partition datasets presented here.

Among the investigated low-temperature treatments, H_2SO_4 leaching gave 56.41% apparent Zn removal from the high-zinc sample but strongly attacked the Ca-bearing matrix. CO_2-assisted leaching gave 31.97% and NaOH only 2.24% under the tested conditions. Thermal pretreatment was route-dependent: 400 °C pretreatment increased subsequent CO_2-assisted removal to 58.40%, whereas 850 °C pretreatment followed by acid leaching gave only 28.28% apparent removal.

Coke addition at intermediate temperatures can increase the relative iron grade without guaranteeing zinc depletion from the retained solid. More effective Zn rejection from the Fe-rich product occurred when strongly reduced or metallic phases were obtained at 1450–1600 °C. The 1600 °C induction product contained 95.5262 wt.% Fe and 3.6854 wt.% C, with Zn below the adopted analytical detection limit (<0.003 wt.% Zn).

For high-zinc Mălina sludge, controlled high-temperature reduction or melting therefore appears to be the most robust route for producing a Zn-depleted Fe-rich metallic product. At the same time, hydrometallurgical treatment may remain useful for selected fractions or as part of an integrated pretreatment strategy. The environmental benefit depends on efficient collection and controlled management of Zn/Pb-bearing leachates, dusts, slags and deposits.

Future work should focus on complete Fe–Zn–Pb mass balances, additional targeted and quantitative XRD analysis combined with SEM–EDS characterization of selected feed and treated products, direct analysis of leachates and furnace dust, and optimization of the balance between treatment intensity, iron recovery, zinc separation, energy demand and management of secondary streams.

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References

ANDERSSON, A., GULLBERG, A., KULLERSTEDT, A., AHMED, H., SUNDQVIST-ÖKVIST, L., SAMUELSSON, C., 2019. *Upgrading of blast furnace sludge and recycling of the low-zinc fraction via cold-bonded briquettes.* J. Sustain. Metall., 5, 350-361.

BESTA, P., JANOVSKÁ, K., SAMOLEJOVÁ, A., BERÁNKOVÁ, A., VOZŇÁKOVÁ, I., HENDRYCH, M., 2013. *The cycle and effect of zinc in the blast-furnace process.* Metalurgija, 52, 197-200.

CANTARINO, M.V., DE CARVALHO FILHO, C., MANSUR, M.B., 2012. *Selective removal of zinc from basic oxygen furnace sludges.* Hydrometallurgy, 111-112, 124-128.

DAS, B., PRAKASH, S., REDDY, P.S.R., MISRA, V.N., 2007. *An overview of utilization of slag and sludge from steel industries.* Resour. Conserv. Recycl., 50, 40-57.

HAMANN, C., SPANKA, M., STOLLE, D., AUER, G., WEINGART, E., AL-SABBAGH, D., OSTERMANN, M., ADAM, C., 2021. *Recycling of blast-furnace sludge by thermochemical treatment with spent iron(II) chloride solution from steel pickling.* J. Hazard. Mater., 402, 123511.

KELEBEK, S., YÖRÜK, S., DAVIS, B., 2004. *Characterization of basic oxygen furnace dust and zinc removal by acid leaching.* Miner. Eng., 17, 285-291.

MANSFELDT, T., DOHRMANN, R., 2004. *Chemical and mineralogical characterization of blast-furnace sludge from an abandoned landfill.* Environ. Sci. Technol., 38, 5977-5984.

STEWART, D.J.C., BARRON, A.R., 2020. *Pyrometallurgical removal of zinc from basic oxygen steelmaking dust: A review of best available technology.* Resour. Conserv. Recycl., 157, 104746.

TRAISTĂ, C., RUS, T., TRAISTĂ, E., 2026. *Pyrometallurgical and Hydrometallurgical Valorization of Blast Furnace Sludge from the Mălina Settling Pond (Galaţi, Romania).* The XXth Balkan Mineral Processing Congress (BMPC 2026), Istanbul, Türkiye, 9-11 April 2026.

TRINKEL, V., MALLOW, O., THALER, C., SCHENK, J., RECHBERGER, H., FELLNER, J., 2015. *Behavior of chromium, nickel, lead, zinc, cadmium, and mercury in the blast furnace: A critical review of literature data and plant investigations.* Ind. Eng. Chem. Res., 54, 11759-11771.

UNITED STATES STEEL CORPORATION, 1985. *The Making, Shaping, and Treating of Steel*. 10th ed. Association of Iron and Steel Engineers, Pittsburgh.

VAN HERCK, P., VANDECASTEELE, C., SWENNEN, R., MORTIER, R., 2000. *Zinc and lead removal from blast furnace sludge with a hydrometallurgical process.* Environ. Sci. Technol., 34, 3802-3808.

WEI, R., ZHANG, F., WANG, X., MENG, D., MENG, K., LONG, H., 2023. *A novel approach for the resource utilization of zinc-bearing dust and sludge via the blast furnace main trough.* Waste Manag., 172, 127-139.

XUE, Y., HAO, X., LIU, X., ZHANG, N., 2022. *Recovery of zinc and iron from steel mill dust: An overview of available technologies.* Materials, 15, 4127.