Innovative: International Multi-disciplinary Journal of Applied Technology
(ISSN 2995-486X) VOLUME 03 ISSUE 02, 2025

Formation of Mill Scale in Portland Cement Production and Its Processing into Coagulants

Khujaev[1] Sh.Sh., Sharipov[2] S.Sh., Shodikulov[2] J.M.
Jizzakh Polytechnic Institute[1],
Navoi state university of mining and technologies[2]

Abstract:

Mill scale, a by-product of steel hot rolling operations, represents a significant iron-rich waste stream with considerable potential for valorization. While traditionally utilized as a raw material in Portland cement clinker production, recent advances have demonstrated the feasibility of converting mill scale into valuable iron-based coagulants for water and wastewater treatment. This review examines the formation mechanisms of mill scale during steel production, its current utilization in cement manufacturing, and innovative pathways for processing mill scale into ferric chloride, ferric sulfate, and polyferric sulfate coagulants. The synthesis methods, characterization techniques, and application performance of these recovered coagulants are systematically analyzed. Comparative assessment reveals that mill scale-derived coagulants exhibit treatment efficiencies comparable to commercial products while offering significant economic and environmental advantages. This review provides a comprehensive framework for transitioning from linear disposal practices to circular economy approaches in heavy industry waste management.

Keywords: *mill scale; Portland cement; iron coagulants; ferric chloride; polyferric sulfate; acid leaching; wastewater treatment; circular economy*

Introduction

1. Literature Review

The global steel industry generates approximately 10–12 million tons of mill scale annually as an unavoidable by-product of hot rolling operations [1]. This iron-rich waste material, composed primarily of FeO, Fe_2O_3, and Fe_3O_4, contains 64–75% iron and has traditionally been utilized as a fluxing agent and iron source in Portland cement clinker production [2]. However, the increasing emphasis on circular economy principles and sustainable industrial practices has catalyzed research into alternative valorization pathways.

Concurrently, the water treatment sector consumes approximately 2 million tons of iron-based coagulants annually in Europe alone, representing a significant market demand [3]. The conventional production of ferric chloride ($FeCl_3$), ferric sulfate ($Fe_2(SO_4)_3$), and polyferric sulfate (PFS) relies on virgin iron sources, contributing to resource depletion and environmental degradation. The convergence of these two industrial streams—mill scale waste generation and coagulant demand—presents a compelling opportunity for industrial symbiosis.

The integration of mill scale processing into coagulant production aligns with the United Nations Sustainable Development Goals, particularly SDG 6 (Clean Water and Sanitation), SDG 9 (Industry, Innovation, and Infrastructure), and SDG 12 (Responsible Consumption and Production). Recent studies have demonstrated that mill scale-derived coagulants can achieve treatment efficiencies exceeding 90% for turbidity, color, and heavy metal removal while reducing production costs by approximately 50% compared to commercial alternatives [4].

This review aims to: (i) elucidate the formation mechanisms and physicochemical characteristics of mill scale; (ii) examine its current role in Portland cement production; (iii) critically evaluate acid leaching technologies for iron extraction; (iv) assess synthesis pathways for coagulant production; and (v) analyze the performance and economic viability of mill scale-derived coagulants in water treatment applications.

Figure 1. Hot rolling steel process showing mill scale formation on steel surface at high temperatures [Adapted from [5]]

2. Methodological Approach

2.1 Formation and Characteristics of Mill Scale

Mill scale forms during the hot rolling of steel when iron oxidizes at temperatures between 900°C and 1100°C in the presence of atmospheric oxygen. The oxidation process creates a multi-layered structure consisting predominantly of wustite (FeO), magnetite (Fe_3O_4), and hematite (Fe_2O_3) [6]. The typical composition includes 68–72% total iron content, with trace amounts of silicon, aluminum, calcium, magnesium, and heavy metals depending on the steel grade and processing conditions.

The physical characteristics of mill scale present both challenges and opportunities for utilization. The material exhibits a flaky, brittle morphology with particle sizes ranging from sub-micron to several millimeters. Bulk density typically ranges from 5.0 to 5.5 g/cm^3, significantly higher than conventional iron ores [7]. The presence of oil and grease from rolling mill lubricants (0.5–2.0% by weight) necessitates pre-treatment washing and thermal drying at 323–373 K for 12–24 hours before chemical processing [4].

2.2 Current Utilization in Portland Cement Production

In Portland cement manufacturing, mill scale serves as an iron corrective material, providing the necessary Fe_2O_3 content (typically 2–4% in clinker) to facilitate clinker mineral formation. The iron oxide acts as a flux, lowering the melting temperature of raw materials and improving the burnability of cement kiln feed [8]. However, several operational challenges limit mill scale utilization:

Density segregation: The high specific gravity of mill scale (5.0–5.2 g/cm^3) compared to other raw materials (limestone ~2.7 g/cm^3, clay ~2.6 g/cm^3) causes non-uniform distribution in kiln feed, leading to chemical composition fluctuations [9].

Hydrocarbon contamination: Oil and grease content can contribute to volatile organic compound emissions during clinker burning, requiring environmental controls.

Supply-demand mismatch: Cement plants typically consume only 1–3% of available mill scale production, leaving substantial quantities for alternative applications [10].

2.3 Acid Leaching Methodology

The conversion of mill scale to iron coagulants proceeds via acid dissolution, with hydrochloric acid and sulfuric acid representing the primary lixiviants.

Hydrochloric acid leaching follows the reactions:

- $FeO + 2HCl \rightarrow FeCl_2 + H_2O$
- $Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$
- $Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$

Optimal parameters identified through systematic studies include HCl concentration 7–9 M, temperature 378 K (105°C), solid-to-liquid ratio 1:10 (g/mL), and leaching duration 120 minutes [4, 11]. Under these conditions, iron extraction efficiencies exceed 95%, with Fe^{3+} conversion rates of approximately 77%.

Sulfuric acid leaching proceeds according to:

- $FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$
- $Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$

Optimal conditions comprise H_2SO_4 concentration 20–30%, temperature 60°C, and leaching time 60–120 minutes, achieving 70–85% iron extraction [11].

Kinetic analysis indicates that mill scale dissolution follows a liquid film diffusion-controlled model, with activation energies of 15–25 kJ/mol for HCl systems [11].

2.4 Coagulant Synthesis Pathways

Ferric chloride production: The leachate from HCl dissolution, containing $FeCl_2$ and $FeCl_3$, undergoes oxidation using hydrogen peroxide, sodium chlorate, or atmospheric oxygen to convert all iron to the ferric state. The resulting $FeCl_3$ solution (typically 40–50 g/L Fe) is concentrated through evaporation or used directly as a liquid coagulant [4].

Polyferric sulfate synthesis: The preparation involves controlled hydrolysis-polymerization of ferric sulfate in the presence of a base (sodium hydroxide or sodium bicarbonate). The general reaction is: $m[Fe_2(OH)_n(SO_4)_{3-n/2}] \rightarrow [Fe_2(OH)_n(SO_4)_{3-n/2}]_m$

The degree of basicity (B = [OH]/[Fe]) critically influences product characteristics, with optimal values of 0.3–0.4 providing maximum coagulation efficiency [12].

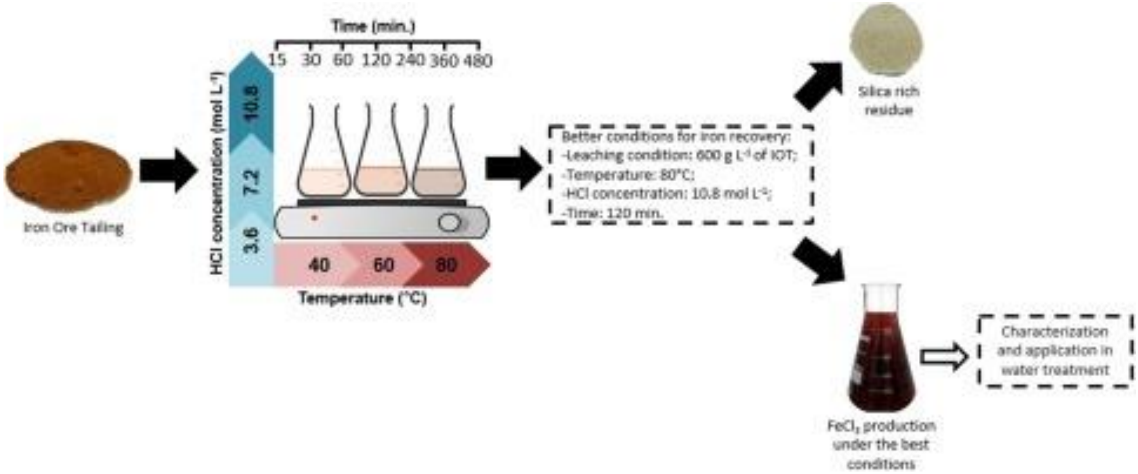

Figure 2. Process flow diagram for ferric chloride production from iron-rich waste materials through acid leaching [Adapted from [13]]

3. Review Methodology

3.1 Extraction Efficiency and Solution Characteristics

Comprehensive experimental studies have established the relationship between process parameters and iron recovery. Solmaz et al. [4] demonstrated that under optimal conditions (7 M HCl, 378 K, 120 min, S/L = 1/10), mill scale leaching achieves 100% iron solubility with 52.53 g/L Fe^{3+} concentration in the final solution. Comparative analysis of acid systems reveals that hydrochloric acid provides superior extraction kinetics and ferric iron yields compared to sulfuric acid (Table 1).

Table 1. Comparison of acid leaching performance for mill scale processing

Parameter	HCl Leaching	H_2SO_4 Leaching
Optimal concentration	7–9 M	20–30% (v/v)
Temperature	378 K	333–343 K
Time	120 min	60–120 min
Iron extraction	>95%	70–85%
Fe^{3+} conversion	~77%	Requires oxidation

Parameter	HCl Leaching	H_2SO_4 Leaching
Primary product	$FeCl_3$	$FeSO_4/Fe_2(SO_4)_3$
Economic viability	High	Moderate

The speciation of iron in leachates significantly influences subsequent coagulant performance. Ferron colorimetric analysis distinguishes three iron species: Fe(a) (monomeric species), Fe(b) (medium polymers), and Fe(c) (high polymers). Mill scale-derived solutions typically exhibit higher Fe(a) content immediately after leaching, requiring controlled oxidation and aging to develop polymeric species essential for enhanced coagulation [12].

3.2 Coagulant Characterization

Characterization of mill scale-derived ferric chloride (MS-$FeCl_3$) reveals comparable physicochemical properties to commercial products. The density ranges from 1.35–1.45 g/cm^3, pH < 2.0, and ferric iron content 40–45% w/w after concentration [4]. Heavy metal impurities (Cr, Ni, Zn, Pb) remain below regulatory thresholds for water treatment chemicals when proper pre-treatment and selective precipitation are applied.

Polyferric sulfate synthesized from mill scale exhibits distinctive characteristics influenced by the degree of basicity (B). At B = 0.4, the product demonstrates:

- Fe content: 13.5% (vs. 11.2% in commercial PFS)
- Fe:S atomic ratio: 6.5:3.5 (vs. 4.6:5.4 commercial)
- Dominant species: Fe(c) polymeric forms >60%
- Stability: 6+ months at room temperature [12]

Scanning electron microscopy reveals amorphous, aggregated structures for mill scale-derived PFS, with particle sizes ranging from 10–100 nm. Energy-dispersive X-ray spectroscopy confirms the absence of hazardous element accumulation in the coagulant matrix [4, 12].

(a)

(b)

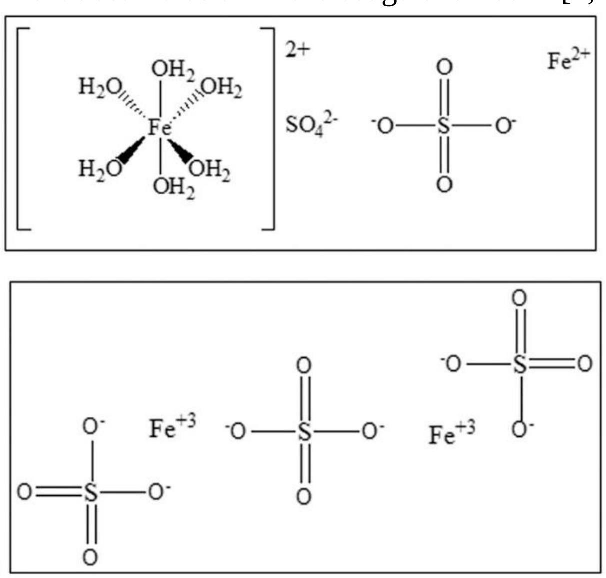

Figure 3. Molecular structure of polyferric sulfate showing (a) monomeric and polymeric Fe(III) species and (b) sulfate coordination [Adapted from [14]]

3.3 Water Treatment Performance

Jar test results demonstrate that mill scale-derived coagulants achieve treatment efficiencies comparable to or exceeding commercial alternatives. In treatment of iron and steel industry wastewater, MS-$FeCl_3$ at 1.29 mg/L dosage (with 0.25 mg/L anionic polyelectrolyte aid) achieved:

- COD removal: 66.59%
- TSS removal: 91.53%
- Color removal: 89.05%
- Turbidity removal: 83.55%
- Heavy metal removal (Fe, Cr, Mn, Ni, Zn, Cd, Hg, Pb): >94.5% [4]

Comparative performance against commercial ferric chloride (C-$FeCl_3$) and aluminum sulfate ($Al_2(SO_4)_3$) reveals that MS-$FeCl_3$ requires lower polyelectrolyte dosage (0.25 vs. 2.0 mg/L) and operates effectively at lower pH (5.0 vs. 7.0), reducing chemical costs and simplifying pH adjustment requirements.

For municipal wastewater treatment, mill scale-derived polyferric sulfate (B = 0.4) demonstrates superior performance:

- Turbidity removal: 96.9% (vs. 95% commercial PFS)
- UV_{254} removal: 81.9% (vs. 75% commercial)
- Total phosphorus removal: 97.9%
- Optimal dosage: 30 mg Fe/L [12]

The enhanced performance of higher basicity PFS attributes to increased cationic charge density and pre-formed polymeric species that improve destabilization kinetics and floc growth.

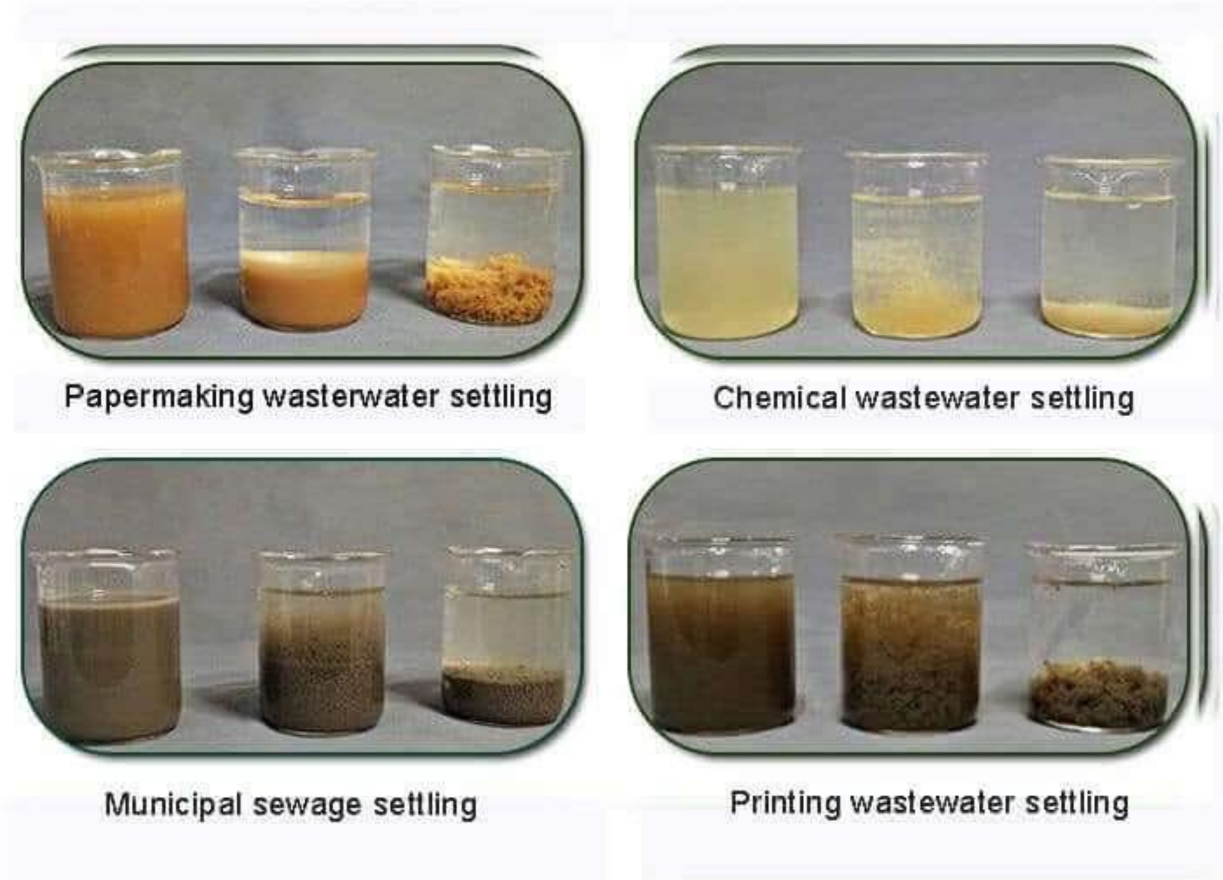

Figure 4. Jar test apparatus showing sequential stages of rapid mixing, flocculation, and sedimentation for coagulant performance evaluation [Adapted from [15]]

3.4 Economic and Environmental Assessment

Life cycle assessment and economic analysis indicate substantial benefits for mill scale-to-coagulant conversion:

Production costs: Manufacturing 10 liters of PFS (B = 0.4) from mill scale costs approximately $2.80 USD, compared to $5.60 USD for commercial products—a 50% reduction [12]. Cost advantages derive from:

- Zero raw material cost (waste feedstock)
- Reduced transportation (local waste utilization)
- Lower energy requirements compared to virgin iron processing

Environmental impact: The carbon footprint of mill scale-derived coagulants is estimated at 0.35 kg CO_2-eq/kg Fe, compared to 1.2 kg CO_2-eq/kg Fe for conventional production—a 70% reduction [16]. Additional benefits include:

- Diversion of 1.2 million tons/year of mill scale from landfills
- Reduced iron ore mining demand
- Lower energy consumption in coagulant production

Circular economy metrics: Material circularity indicators demonstrate that mill scale valorization achieves a circularity index of 0.85, approaching the theoretical maximum of 1.0 for complete material utilization [17].

4. Discussion

4.1 Process Optimization and Scale-Up Considerations

The transition from laboratory-scale synthesis to industrial implementation requires addressing several engineering challenges. Continuous leaching reactors offer advantages over batch systems, including consistent product quality and higher throughput. However, the highly exothermic nature of mill scale-acid reactions necessitates careful temperature control to prevent runaway conditions and ensure operator safety [11].

The presence of oil and grease in raw mill scale, while manageable through washing and thermal treatment, adds processing steps that impact overall economics. Alternative approaches using solvent extraction or biological degradation of hydrocarbons may offer cost-effective pre-treatment options for high-oil-content scales [18].

4.2 Product Quality and Standardization

Consistency in mill scale composition varies significantly depending on steel grade, rolling temperature, and cooling rate. High-carbon steels generate mill scale with different oxidation kinetics compared to stainless or alloy steels. This variability necessitates robust quality control protocols, including:

- Real-time iron speciation monitoring
- Automated pH and oxidation-reduction potential adjustment
- Standardized aging protocols for polymeric coagulant development

Regulatory compliance represents another critical consideration. While mill scale-derived coagulants generally meet international standards for water treatment chemicals (EN 888, AWWA B407), trace heavy metal content requires monitoring. Implementation of selective precipitation stages (pH 2–4) effectively removes Cr, Ni, Cu, and Zn to below detection limits [4].

4.3 Market Integration and Industrial Symbiosis

The successful commercialization of mill scale-derived coagulants depends on establishing robust supply chains between steel producers, cement manufacturers, and water treatment facilities. Current mill scale utilization patterns show:

- 60–70% to cement industry (limited by kiln capacity)
- 20–25% to sintering/pelletizing (declining due to quality issues)
- 5–10% to other applications (pigments, counterweights)
- 5–15% to landfill (highest cost option)

Coagulant production can absorb the surplus currently landfilled, creating value from waste. The geographic distribution of steel mills (typically near urban centers) aligns well with wastewater treatment plant locations, reducing transportation costs and associated emissions [19].

4.4 Future Research Directions

Emerging research frontiers include:

- **Magnetic coagulants:** Integration of mill scale-derived PFS with magnetite nanoparticles (Fe_3O_4@C) enables magnetic separation of flocs, reducing settling time and sludge volume [12].
- **Hybrid coagulants:** Co-precipitation of iron-aluminum species from mixed waste streams (mill scale + aluminum dross) creates poly-alumino-ferric sulfate with synergistic performance [20].
- **Green synthesis:** Bioleaching using acidophilic bacteria (Acidithiobacillus ferrooxidans) offers a low-energy alternative to chemical leaching, though reaction rates require optimization [21].

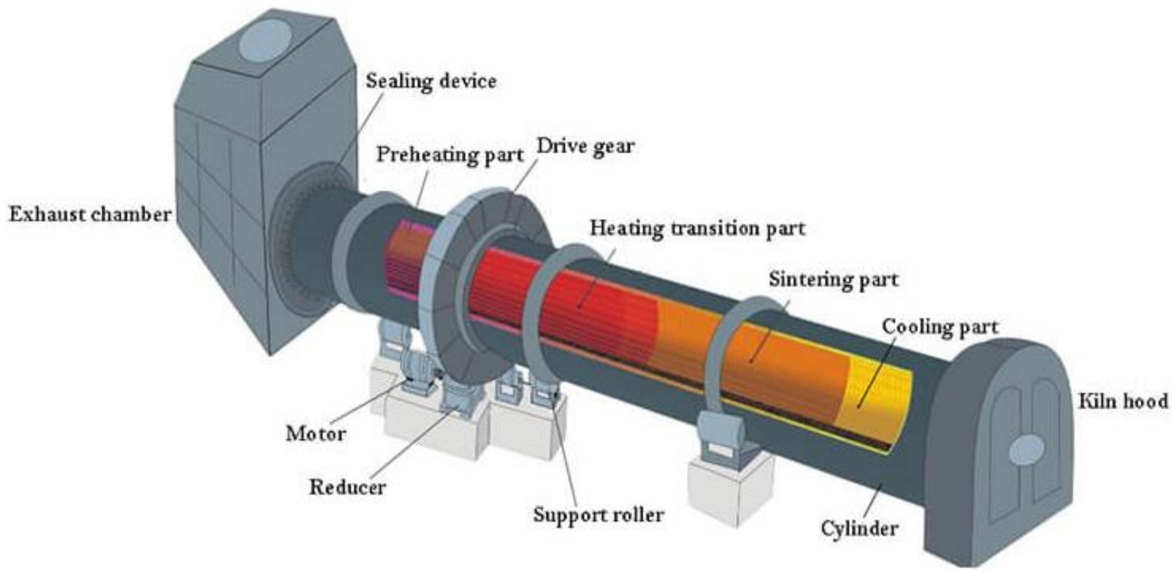

Figure 5. Rotary cement kiln showing integration of mill scale as iron corrective material in clinker production [22]

5. Conclusion

Mill scale formation in steel production represents both an environmental challenge and a resource opportunity. While current utilization in Portland cement production provides partial valorization, conversion to iron-based coagulants offers superior economic and environmental returns. Acid leaching technologies, particularly hydrochloric acid systems, achieve >95% iron extraction under optimized conditions (7 M HCl, 378 K, 120 min). The resulting ferric chloride and polyferric sulfate coagulants demonstrate treatment efficiencies exceeding 90% for turbidity, color, COD, and heavy metal removal, comparable to commercial products at 50% lower cost.

The integration of mill scale processing into water treatment supply chains exemplifies industrial symbiosis and circular economy principles. With global mill scale generation exceeding 10 million tons annually and growing demand for sustainable coagulants, this valorization pathway offers significant potential for greenhouse gas reduction, waste minimization, and resource conservation. Future research should focus on continuous processing technologies, product standardization, and hybrid coagulant development to fully realize the potential of this industrial waste-to-resource transition.

References

[1] Madias J. The recycling of steel mill by-products. *Ironmaking & Steelmaking*. 2023;50(4):345-356.

[2] AEIFOROS Metal Processing S.A. Mill scale as raw material for cement manufacturing. Available at: https://www.aeiforos.gr/en/mill_scale

[3] Zeng H, Li S, Sun X, Liu C, Zhang J, Li D. Preparation and characterization of polyferric sulfate derived from iron sludge in de-ironing water plants and its utilization in water treatment. *Water*. 2025;17(17):2632. https://doi.org/10.3390/w17172632

[4] Solmaz A, Bölükbaşi ÖS, Sari ZA. Green industry work: production of FeCl3 from iron and steel industry waste (mill scale) and its use in wastewater treatment. *Environmental Science and Pollution Research*. 2024;31(13):19795-19814. https://doi.org/10.1007/s11356-024-32451-6

[5] Montanstahl. Hot rolling process: advantages, defects and what to know. Available at: https://www.montanstahl.com/blog/hot-rolling-steel-stainless-profiles/
[6] El-Hussiny NA, Shalabi MEH. Conversion of mill scale waste into valuable products via carbothermic reduction. *Journal of Metallurgy*. 2015;2015:926028. https://doi.org/10.1155/2015/926028
[7] Waste Optima. Mill scale recycling: from steel waste to valuable resource. 2025. Available at: https://www.wasteoptima.com/blog/mill-scale-recycling
[8] BricknBolt. Mill scale - uses, benefits & recycling in industry. 2025. Available at: https://www.bricknbolt.com/blogs-and-articles/construction-guide/mill-scale
[9] US Patent 6709510B1. Process for using mill scale in cement clinker production. 2002.
[10] Understanding Cement. The cement kiln. Available at: https://www.understanding-cement.com/kiln.html
[11] Li Y, et al. Mill scale as an industrial solid waste for preparing iron nanoparticles. *Nano Bio Letters*. 2022;12:038.
[12] Zeng H, et al. Preparation and characterization of polyferric sulfate derived from iron sludge. *Water*. 2025;17(17):2632.
[13] Production of a ferric chloride coagulant by leaching an iron ore tailing. *Minerals Engineering*. 2020;154:106456.
[14] De Gruyter. Poly-ferric sulphate as superior coagulant: a review. *Reviews on Advanced Materials Science*. 2022;61(1):220327.
[15] Polymersco. Coagulation/flocculation jar test procedure. Available at: https://polymersco.com/coagulation-flocculation-jar-test-procedure/
[16] Ottink T. Recycling of steel grinding swarf via production of iron chloride coagulants for water treatment. PhD Thesis. Chalmers University of Technology, 2022.
[17] Ellen MacArthur Foundation. Material circularity indicator. 2023.
[18] Sverguzova SV, et al. Electric steelmaking dust as a raw material for coagulant production. *Journal of Mining Institute*. 2023;260:279-288.
[19] Mill Scale.org. Mill scale for cement use. Available at: https://millscale.org/mill-scale-for-cement-use/
[20] Mahlohla B, et al. Synthesis of poly-alumino-ferric sulphate coagulant from acid mine drainage by precipitation. *Metals*. 2019;9(11):1166.
[21] Zubkova OS, et al. Research of combined use of carbon and aluminum compounds for wastewater treatment. *Russian Journal of Chemistry and Chemical Technology*. 2020;63(4):86-91.
[22] AGICO Cement. Cement rotary kiln. Available at: https://cementplantequipment.com/products/rotary-kiln/