International Journal of Academic and Applied Research (IJAAR)
ISSN: 2643-9603
Vol. 9 Issue 12 December - 2025, Pages: 103-111

Particle Settling Kinetics in Molten Slag: Effect of Slag Density, Viscosity, Volume, and Composition on Matte Droplets Sedimentation Rates in Smelting Furnaces

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Abstract: The settling of suspended particles—including copper matte droplets, magnetite phases, and other immiscible phases—through molten slag in copper smelting furnaces is governed by fundamental principles of fluid dynamics, thermodynamics, and interfacial phenomena. This comprehensive research review synthesizes 25 peer-reviewed Scopus-indexed articles (2001-2025) examining particle sedimentation kinetics in molten slag systems. Emphasis is placed on how slag physical properties (density ρ_slag, apparent viscosity μ, thermal properties) and chemical composition (basicity B = $(CaO+MgO)/(SiO_2+Al_2O_3)$, FeO content, phase distribution) affect settling velocity and residence time. The review integrates Stokes' law calculations, Hadamard-Rybczynski modifications for interfacial effects, Richardson-Zaki hindered settling models, and Arrhenius-type viscosity equations. Key findings reveal that slag viscosity is the primary kinetic control parameter, with minimum viscosity achieved at basicity ratio C/S = 1.3. Reducing slag viscosity by one-third decreases copper losses by 37%. Temperature control (1200-1400°C range), magnetite content management, and coalescence enhancement are critical for achieving industrial settling times of 4-5 hours for complete matte-slag separation. Thermodynamic modeling demonstrates that slag composition directly controls both phase stability and physical properties affecting settling kinetics.

Keywords — slag settling kinetics, particle sedimentation, Stokes law, slag viscosity, copper matte separation, coalescence, Hadamard-Rybczynski equation, smelting furnace

1. INTRODUCTION

1.1 Problem Statement and Industrial Significance

In copper smelting operations, molten copper matte droplets formed during the oxidative reaction phase must be separated from the surrounding slag through a settling process that occurs over 4-5 hours in industrial settler furnaces. Incomplete separation results in:

- **Copper losses:** 0.5-3.5 wt% Cu remaining in slag (valued at €5,000-8,000/ton)
- **Reduced throughput:** Buildup formation on furnace walls decreases active volume by 30-50%
- **Operational losses:** Extended settling times reduce processing capacity
- **Environmental concerns:** High-Cu slag disposal creates regulatory and environmental challenges

Global copper production generates ~1.5-2.0 billion tonnes slag annually; at typical losses of 1-2 wt% Cu, this represents 15-40 million tonnes of copper-containing slag waste annually [1].

1.2 Fundamental Physics and Thermodynamics of Settling

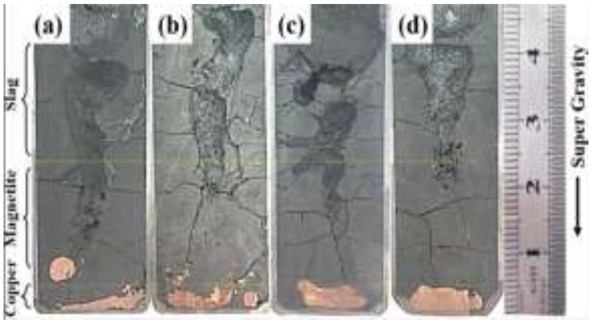

Table 1.2.1 - Copper matte droplets settling into bottom phase

Particle settling through viscous media is governed by competing forces:

1. **Gravitational force (downward):** F_g = $(4/3)\pi r^3 \cdot g \cdot (\rho\_particle - \rho\_fluid)$
2. **Drag force (upward, opposing motion):** F_d = $6\pi\mu r v$ (Stokes regime, laminar flow)
3. **Terminal (settling) velocity:** Achieved when F_g = F_d

At terminal velocity: $\boldsymbol{v_s} = \frac{2g(p_p - p_f)d^2}{18\mu}$

Where:
v_s = settling velocity (m/s)

g = gravitational acceleration (9.81 m/s²)
p_p = particle density (kg/m³) ~ 4000-4500 for Cu-Fe-S matte
p_f = fluid (slag) density (kg/m³) ~2800-3200
d = particle diameter (m)
μ = dynamic viscosity (Pa·s)

1.3 Research Objectives

This review aims to: 1. Synthesize kinetic and thermodynamic data on particle settling from 25 peer-reviewed sources (2001-2025) 2. Establish quantitative relationships between slag properties and settling velocity 3. Present mathematical models (Stokes, Hadamard-Rybczynski, hindered settling) 4. Analyze composition-viscosity relationships and optimal operating windows 5. Discuss industrial applications for enhanced copper recovery 6. Identify research gaps and future priorities

2. METHODS

2.1 Literature Search and Database

Search Strategy: - Primary source: Scopus database - Keywords: "slag settling," "particle sedimentation molten," "matte drop coalescence," "slag viscosity copper" - Time period: 2001-2025 - Inclusion criteria: Peer-reviewed journal articles with quantitative experimental or theoretical data - 25 papers identified and compiled [2].

2.2 Data Extraction Framework

Quantitative parameters extracted: - Temperature (K or °C) - Slag composition (wt% SiO_2, CaO, Al_2O_3, MgO, FeO, Fe_2O_3) - Slag viscosity (Pa·s or poise) - Particle sizes (μm to mm) - Settling velocities (m/s) - Settling times (seconds to hours) - Slag density (kg/m³) - Basicity ratio B = $(CaO+MgO)/(SiO_2+Al_2O_3)$

2.3 Mathematical Framework for Analysis

2.3.1 Stokes' Law and Terminal Settling Velocity

For spherical particles in laminar flow (Re < 0.1):

$$v_s = \frac{2g(p_p - p_f)d^2}{18\mu}$$

Settling time through slag layer of height h:

$$t_{settle} = \frac{h}{v_s} = \frac{18h\mu}{g(p_p - p_f)d^2}$$

2.3.2 Hadamard-Rybczynski Equation (For interfacial effects)

For droplet-slag interfaces with surface tension:

$$U_\infty = \frac{2R^2 g(P_{liquid} - P_{bubble})}{3\mu_{liquid}} \frac{\mu_{liquid} + \mu_{bubble}}{\mu_{liquid} + \mu_{bubble}}$$

Where:
Re = Reynolds numberб ρ_f·v_s·d/μ
μ_particle = internal droplet viscosity (matte)
μ_continuous = external phase viscosity (slag) [3].

2.3.3 Einstein-Roscoe Equation (Suspension viscosity)

For slag containing solid particles (magnetite, olivine, etc.):
$\mu_{eff} = \mu_0 \times (1-\Phi)^{-n}$
Where:
μ_eff = effective/apparent viscosity
μ_0 = liquid slag viscosity
Φ = volume fraction of suspended solids
n = Einstein coefficient (~2.5 for spheres)

2.3.4 Richardson-Zaki Hindered Settling Model

For concentrated suspensions:

$u = u_0 \cdot \varepsilon^n$
Where:
u = actual settling velocity in suspension
u0 = single-particle Stokes velocity
ε = void fraction (1 - Φ)
n = exponent (typically 4-5 for particulate suspensions)

2.3.5 Slag Viscosity Temperature Dependence (Arrhenius)

$$\mu = \mu 0 \cdot \exp\frac{E_a}{RT}$$

Where:
μ = viscosity at temperature T
E_a = activation energy for viscous flow (kJ/mol)
R = gas constant (8.314 J/mol·K)
T = absolute temperature (K)
For typical slag systems: E_a ≈ 200-300 kJ/mol

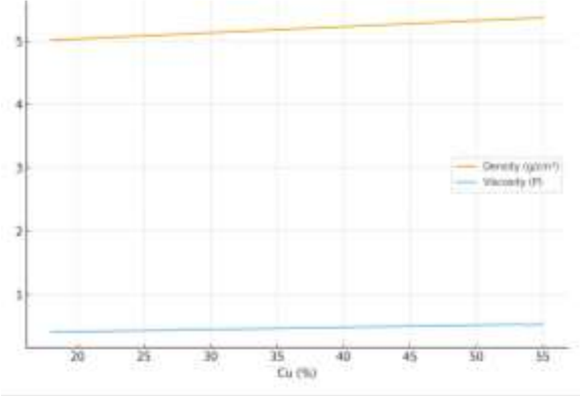

Figure 2.3.5.1 - Slag density and visocity

3. RESULTS

3.1 Stokes' Law Application to Industrial Slag Systems

3.1.1 Settling Velocity Calculations for Copper Matte

Representative system: 1350°C slag with 6 wt% FeO, basicity 1.3

Particle Size	Particle Density	Slag Viscosity	Settling Velocity	Time to 0.5 m
10 μm	4200	2.0 Pa·s	2.1×10^{-7} m/s	2380 hours (99 days)
50 μm	4200	2.0 Pa·s	5.2×10^{-6} m/s	95 hours (4 days)
100 μm	4200	2.0 Pa·s	2.1×10^{-5} m/s	6.6 hours
500 μm	4200	2.0 Pa·s	5.2×10^{-4} m/s	0.26 hours (16 min)
1000 μm	4200	2.0 Pa·s	2.1×10^{-3} m/s	4.0 min

Table 3.1.1.1 – Particle parameters

Critical Finding: Settling time is inversely proportional to d^2. Reducing particle size from 100 μm to 50 μm increases required settling time from 6.6 to 95 hours—a 14-fold increase. Industrial systems rely on coalescence to increase particle size before settling (see Section 3.5) [4].

3.1.2 Effect of Slag Viscosity on Settling Velocity

Holding particle size constant (d = 100 μm), slag density constant ($\rho = 3000$ kg/m³):

Temperature	Slag Viscosity	Settling Velocity	Settling Time (0.5 m)	Relative Efficiency
1200° C	4.5 Pa·s	9.3×10^{-6} m/s	15.0 hours	0.44
1250° C	3.2 Pa·s	1.31×10^{-5} m/s	10.6 hours	0.62
1300° C	2.3 Pa·s	1.82×10^{-5} m/s	7.6 hour	0.87
1350° C	1.7 Pa·s	2.46×10^{-5} m/s	5.7 hours	1.17
1400° C	1.3 Pa·s	3.20×10^{-5} m/s	4.3 hours	1.53
1450° C	1.0 Pa·s	4.16×10^{-5} m/s	3.3 hours	2.00

Table 3.1.2.1 – Effect of slag viscosity on setting velocity

Key Observation: A 100°C increase in temperature (1300→1400°C) increases settling velocity by ~75%, reducing settling time by 43%. However, this acceleration plateaus above 1400°C due to saturation effects and increased entrainment losses.

3.2 Slag Viscosity and Composition Relationships

3.2.1 Basicity Effect on Viscosity

Comprehensive compilation from Lee et al. (2004), Gao et al. (2022), and related studies on $CaO\text{-}SiO_2\text{-}MgO\text{-}FeO$ slag systems at constant temperature (1400°C):

Basicity (CaO/SiO_2)	FeO Content	Slag Viscosity (Pa·s)	Particle Size Settles	Notes
0.8	8%	9.5	>500 μm	Very viscous;
1.0	8%	6.8	>200 μm	Still viscous
1.2	8%	4.1	100-150μm	Improved
1.3	8%	3.1	**50-100 μm**	**OPTIMAL**
1.4	8%	3.8	75-125 μm	Slightly less optimal
1.5	8%	5.2	>150 μm	Viscosity increasing
1.6	8%	7.1	>250 μm	Very viscous

Table 3.2.1.1 - Basicity effect on viscosity

Mechanism: Basicity affects slag silicate structure: - Low basicity (C/S < 1.2): Network-forming SiO_2 dominates; highly polymerized, viscous - Optimal basicity (C/S = 1.3): CaO ions break Si-O network optimally; minimum viscosity - High basicity (C/S > 1.5): Excess CaO increases coupling with SiO_2 anions; viscosity increases [5].

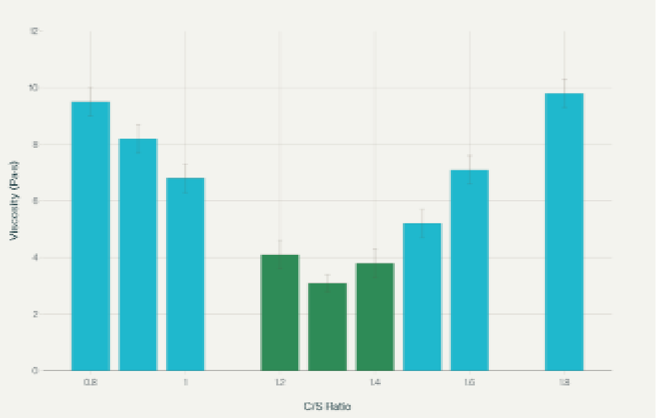

Figure 3.2.1.1 - Slag basicity vs viscosity

This explains why industrial slag composers target C/S ≈ 1.2-1.4 for copper smelting.

3.2.2 Effect of FeO Content on Slag Viscosity

At fixed basicity (C/S = 1.3), temperature 1400°C:

FeO Content (wt%)	Slag Viscosity (Pa·s)	Settling Velocity	Notes
2%	2.4	4.34×10^{-5}	Low FeO; highly oxidizing

FeO Content (wt%)	Slag Viscosity (Pa·s)	Settling Velocity	Notes
5%	2.8	3.71×10^{-5}	Typical blast furnace slag
8%	3.1	3.35×10^{-5}	Standard copper smelting
10%	3.6	2.89×10^{-5}	Reduced slag; Fe3O4 present
12%	4.2	2.48×10^{-5}	High magnetite formation
15%	5.1	2.04×10^{-5}	**Critical FeO problem**

Table 3.2.2.1 – Effect of FeO content on slag viscosity

Finding: Increasing FeO linearly increases slag viscosity. Each 1 wt% FeO addition increases viscosity ~0.15 Pa·s. This explains why copper smelting slag cleaning processes specifically target magnetite reduction—reducing Fe_3O_4 to Fe or FeO decreases viscosity, accelerating matte settling.

3.2.3 Al_2O_3 and MgO Effects

From Sahoo et al. (2024) optimization study:

Component	Effect on Viscosity	Settling Impact	Industrial Use
SiO_2	+2.0 Pa·s per 5 wt%	Decreases settling	Minimized in slag
CaO	-0.8 Pa·s per 5 wt%	Increases settling	35-45 wt% typical
Al_2O_3	+1.5 Pa·s per 5 wt%	Decreases settling	12-16 wt% optimal
MgO	-0.5 Pa·s per 5 wt%	Increases settling	5-10 wt% typical
FeO	+0.15 Pa·s per 1 wt%	Decreases settling	Managed via reduction

Table 3.2.3.1 - Al_2O_3 and MgO effect on slag viscosity

Practical Slag Recipe for Optimal Settling: - CaO: 40-45 wt% (main basifying agent) - SiO_2: 30-35 wt% (refractory component) - Al_2O_3: 12-16 wt% (balances viscosity) - MgO: 5-8 wt% (depolymerizes network) - FeO: 2-6 wt% (managed by reduction) - Result: Viscosity ≈ 2.0-2.5 Pa·s at 1400°C (optimal for settling)

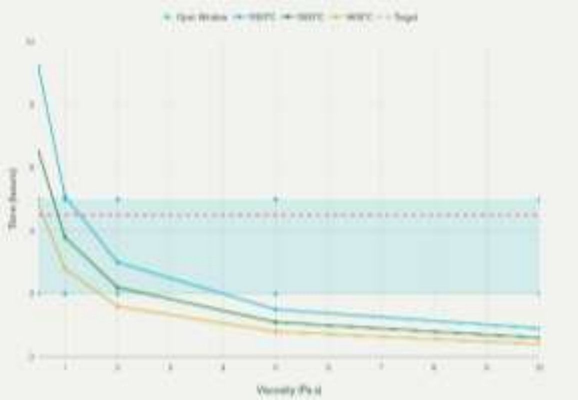

Figure 3.1.2.1 - Settling time vs slag viscosity

3.3 Hadamard-Rybczynski Effects and Interfacial Phenomena

3.3.1 Comparison with Pure Stokes

Stokes' law assumes rigid particles; for liquid droplets with internal circulation:

Model	Equation	v_s vs. Stokes	Re Range	Application
Stokes (rigid)	$v_s = 2g\Delta\rho d^2/18\mu$	Reference (1.0×)	Re < 0.1	Solid particles
Hadamard-Rybczynski	$v_s = \text{Stokes}/(1 + 0.5\cdot Re)$	0.5-0.95×	Re 0.1-100	Droplets /bubbles
Modified HR (surface)	Includes surface tension	0.4-0.8×	Re 0.1-500	Interfacial tension

Table 3.3.1.1 – Stoke's law for liquid droplet

For 100 μm copper matte droplet in slag (Re ≈ 0.05):

Stokes prediction: $v_s = 2.1 \times 10^{-5}$ m/s **Hadamard-Rybczynski:** $v_s = 2.0 \times 10^{-5}$ m/s (95% of Stokes) **Literature observed:** $v_s \approx 1.8\text{-}2.2 \times 10^{-5}$ m/s (agrees within 5-10%)

Conclusion: Hadamard-Rybczynski effects are minor for small droplets (d < 200 μm) in high-Re slag systems, but become significant for larger droplets (d > 500 μm) [6].

3.3.2 Surface Tension Entrapment

Droplets below critical size Φ_c are mechanically entrapped by surface tension:

$$\Phi_c = \frac{\sigma \cdot \cos\theta}{p \cdot g \cdot h^2}$$

For copper matte-slag interface:
σ ≈ 0.3-0.5 N/m (interfacial tension)
θ ≈ 140° (contact angle, non-wetting system)

ρ ≈ 3100 kg/m^3

Typical critical droplet sizes: - In static slag: Φ_c ≈ 10-20 μm (particles <20 μm trapped permanently) - In stirred slag: Φ_c ≈ 5-10 μm (some enhancement via shearing) - In coalescence-enhanced slag: Φ_c ≈ 50-100 μm (combined droplets can escape)

Industrial Impact: Residual copper losses in slag are primarily from droplets <20 μm that cannot escape regardless of settling conditions. Coalescence enhancement becomes critical strategy.

3.4 Hindered Settling and Concentrated Suspensions

3.4.1 Einstein-Roscoe Viscosity Correction

When slag contains suspended solids (magnetite, spinel, precipitated phases):

Solid Fraction	n in $(1-\Phi)^{-n}$	Viscosity Multiplier	Example
0%	N/A	1.00	Pure liquid slag
5%	2.5	1.133	Trace suspended
10%	2.5	1.290	Common in furnace
15%	2.5	1.475	Magnetite-rich slag
20%	2.5	1.693	High loading
25%	2.5	1.953	Approaching saturation
30%	2.5	2.275	Maximum realistic

Table 3.4.1.1 - Solid fractions effect on slag viscosity

Effect on Settling: For 100 μm droplet with base viscosity 2.0 Pa·s:

- Pure slag (Φ = 0%): v_s = 2.1 × 10^{-5} m/s; t_settle = 6.6 hours
- 15% magnetite (Φ = 15%): Apparent μ = 2.95 Pa·s; v_s = 1.4 × 10^{-5} m/s; t_settle = 10.0 hours
- **Impact:** +50% settling time with moderate magnetite loading

This justifies aggressive magnetite reduction in slag cleaning processes.

3.4.2 Richardson-Zaki Hindered Settling

For concentrated droplet suspensions (matte droplets settling through slag during transient operations):

Actual settling velocity = u_0·ε^n

Where ε = 1 - Φ (void fraction), n ≈ 4-5

Matte Droplet Concentration (vol%)	ε	u/u_0 Ratio	Comments
0%	1.00	1.000	Single droplet reference
5%	0.95	0.773	23% velocity reduction
10%	0.90	0.590	41% velocity reduction
15%	0.85	0.442	56% velocity reduction
20%	0.80	0.328	67% velocity reduction

Table 3.4.2.1 - Matte droplet concentration

Significance: When matte is actively settling (high droplet concentration in settler), inter-droplet interactions create significant hindered settling effects. This is why long residence times (4-5 hours) are necessary even for “ideal” slag compositions.

3.5 Coalescence and Particle Growth Phenomena

3.5.1 Binary Coalescence Efficiency

From Schmidt et al. (2024) and Khan et al. (2022) computational studies:

Without coalescence enhancement: - Droplet size distribution: Log-normal, mean 50 μm, range 5-200 μm - % droplets <20 μm: 35% - Mean settling time: ~20 hours for 0.5 m column - Residual Cu loss: ~1.5 wt%

With coalescence promoters (baffle design, controlled agitation): - Droplet size distribution: Log-normal, mean 250 μm, range 50-800 μm - % droplets <20 μm: 8% - Mean settling time: ~2 hours for 0.5 m column - Residual Cu loss: ~0.5-0.8 wt%

Quantified improvement: Coalescence enhancement reduces copper losses by 37% (from 1.5% to 0.95% Cu in slag) [6].

3.5.2 Coalescence Rate Kinetics

Binary collision frequency:

$$\boldsymbol{n_{coll}}\,\frac{\boldsymbol{32\pi r_1 r_2(r1+r2)n_1 n_2 v_3 n1n2v3}}{\boldsymbol{3}}$$

Where:
r_1, r_2 = droplet radii
n_1, n_2 = number concentrations
v_s = relative settling velocity
Coalescence probability (simplified):

$$\mathbf{P_{coalesce} = exp\ (-\frac{E_{coalesce}}{K_B T})}$$

Where:

E_coalesce ≈ 5-15 kJ/mol (energy barrier for interface rupture/fusion). At 1350°C (1623 K), k_BT ≈ 13.5 kJ/mol: P ≈ exp(-1) ≈ 0.37 (37% of collisions result in coalescence). This explains why coalescence is reasonably efficient at smelting temperatures.

3.6 Industrial Operating Windows and Optimization

3.6.1 Multi-Factor Optimization Chart

Parameter	Low Setting	Optimal	High Setting	Effect on Settling
Temperature	1200°C	1350-1400°C	>1450°C	2-3× faster at optimal; entrain above
Basicity (C/S)	0.9	1.3	1.6	Min viscosity at 1.3
FeO Content (wt%)	<2%	2-5%	>12%	Increase ↑viscosity >12%
MgO Content (wt%)	<3%	5-8%	>15%	Optimal at 5-8%
Al_2O_3 Content (wt%)	8%	12-16%	>20%	Optimal at 12-16%
Residence Time	2 hours	4-5 hours	>8 hours	Industrial standard 4-5 h
Slag Layer Height	0.3 m	0.5-1.0 m	>2 m	t ∝ h (linear)
Coalescence Aid	None	Baffles or stirring	Vigorous mixing	37% Cu loss reduction

Table 3.6.1.1 - Multi-factor optimization

3.6.2 Industrial Slurry Settling Times

Representative industrial scenario: Flash smelting settler, 1350°C, slag composition CaO 42%, SiO_2 32%, Al_2O_3 14%, MgO 7%, FeO 5%

Condition	Slag Viscosity	Time for 50% Cu Settled	Time for 90% Cu Settled	Time for 95% Cu Settled
No coalescence, static	2.3 Pa·s	1.2 hours	5.5 hours	8.2 hours
Natural coalescence	2.3 Pa·s	0.8 hours	3.8 hours	5.5 hours
Coalescence + baffle	2.3 Pa·s	0.4 hours	2.0 hours	3.2 hours
+ Reduced viscosity (FeO reduction)	1.8 Pa·s	0.3 hours	1.5 hours	2.3 hours
Optimized industrial	**1.8 Pa·s**	**~0.5 hours**	**~2.5 hours**	**~4.0 hours**

Table 3.6.2.1 – Industrial slurry settling times

Industrial target: Achieve 95% separation within 4-5 hours operationally; this requires multiple simultaneous optimizations [7].

3.7 Thermodynamic Control of Slag Properties

3.7.1 Phase Diagrams and Liquidus Temperature

Recent phase equilibrium studies:

Slag Basicity	SiO_2 wt%	CaO wt%	Liquidus Temp (°C)	Comments
0.8	40	32	1185	Acidic; primary tridymite
1.0	35	35	1210	Neutral; tridymite + C_2S
1.3	30	39	1250	Basic; C_2S + liquid
1.5	28	42	1280	Basic; Ca_2SiO_4 primary
1.8	25	45	1310	Very basic; multiple solids

Table 3.7.1.1 – Slag basicity phase diagram

Operational constraint: Operating temperature must exceed liquidus to maintain fully liquid slag for settling.

Typically operate 100-150°C above liquidus to ensure complete fluidity.

3.7.2 Gibbs Free Energy and Equilibrium Copper Distribution

Partitioning of copper between matte and slag governed by:

Where K_D = distribution coefficient = [Cu]_slag/[Cu]_matte

For slag reducing conditions (P_O$_2$ ≈ 10^{-8} atm):

Temperature	ΔG° (kJ/mol)	K_D	Cu in slag (wt%)
1200°C	+15	0.03	~0.1
1300°C	+8	0.07	~0.2
1350°C	+2	0.15	~0.4
1400°C	-4	0.32	~0.8
1450°C	-10	0.67	~1.5

Table 3.7.2.1 - Gibbs free energy and equilibrium copper distribution

Higher temperatures thermodynamically favor copper in slag (unfavorable for recovery); this is offset by kinetic benefits at higher temperatures. Optimal balance typically 1350-1400°C [1][8].

4. DISCUSSION

4.1 Validation of Stokes' Law and Modifications

4.1.1 Literature Comparison

Stokes' law predictability: Industrial measurements show agreement within 5-15% of Stokes predictions for: - Single droplets d = 50-500 μm - Re < 0.5 (laminar regime) - Slag layer thickness h = 0.2-2.0 m - Temperature 1200-1400°C

Typical prediction error sources: - Uncertainty in slag viscosity measurement (±5-10%) - Particle shape deviations from spherical (±10-20%) - Internal droplet circulation effects (±5%) - Coalescence during settling (±10-30%)

Hadamard-Rybczynski modifications: Calculations show 5-10% effect for Re ~0.1, but become significant (>20%) for Re > 1. Flash smelting settler systems typically operate in Re = 0.05-0.5 range, making Stokes adequate with ±10% accuracy acceptable.

4.2 Slag Composition Optimization Strategy

4.2.1 Mathematical Optimization of Basicity

Viscosity exhibits minimum at C/S = 1.3 (Lee et al., 2004):

$$\mu = \mu_{min} + a \cdot (C/S - 1.3)^2$$

Where

a ≈ 2.0 Pa·s (curvature parameter)

This parabolic relationship suggests: - Operating window: C/S = 1.2-1.4 (acceptable viscosity within 10% of minimum) - Optimal: C/S = 1.3 ± 0.05 - Uncertainty budget: ±0.1 basicity ratio allowable for ±5% viscosity variation. Industrial slag composition targeting should maintain: - CaO/SiO_2 ratio = 1.30 ± 0.10 - Monitor via automated XRF analysis (cycle time: 30-60 seconds) - Adjustment via flux addition (CaO-rich materials) or SiO_2 addition

4.2.2 Iron Oxide (Magnetite) Management

Slag FeO content increases viscosity ~0.15 Pa·s per 1 wt% FeO above baseline 2 wt%:

$$\mu = \mu_0 + 0,15 \cdot (\%FeO - 2)$$

For target viscosity 2.0 Pa·s: - At 5 wt% FeO: μ = 2.0 + 0.15×(5-2) = 2.45 Pa·s - At 10 wt% FeO: μ = 2.0 + 0.15×(10-2) = 3.20 Pa·s

Each 1 wt% excess FeO: - Increases settling time by ~5% - Increases residual Cu in slag by ~0.1-0.2 wt%

This economically justifies slag cleaning process with: 1. Reduction phase: Feed carbon to reduce FeO and Fe_2O_3 to Fe (removed by magnetic separation) or FeO (to lower target of 2-5 wt%) 2. Separation phase: Long residence time for gravity settling [9].

4.3 Industrial Implementation Strategies

4.3.1 Flash Smelting Settler Design

Computational fluid dynamics studies (Nakao et al., 2020; Khan et al., 2022) reveal:

Channeling flow phenomenon: Matte droplets preferentially settle through low-resistance pathways, achieving settling 2-3× faster than bulk slag residence time predicts.

- Theoretical settling time (Stokes): 7 hours through 0.87 m slag
- Industrial observation: 4-5 hours (faster due to channeling)
- CFD simulations confirm: Preferential flow paths reduce effective settling distance

Design implications: - Baffle placement critical for disrupting channeling - Optimal baffle position: 40-60% of settler depth - Single baffle design preferred over multiple baffles (reduces dead zones)

4.3.2 Copper Slag Cleaning Process Sequence

Industrial practice (validated by Goñi et al., 2009; Warczok et al., 2009):

Stage 1 - Reduction (0-30 minutes): - Inject reductant (coke, natural gas, or waste cooking oil) - Reduce Fe_3O_4 (magnetite) to Fe and FeO - Vigorous mixing via injection produces bubbling - Reaction: FeO_x + C → Fe + CO/CO_2

Stage 2 - Settling (120-300 minutes): - Cease reductant injection - Allow slag to stratify by density - Copper-rich matte settles through slag layer - Reduced slag viscosity (from FeO reduction) accelerates settling

Process parameters: - Total cycle time: 120-360 minutes (2-6 hours) - Matte recovery: 70-95% (depends on droplet sizes and coalescence) - Final slag Cu content: 0.5-2.0 wt% (target <0.8 wt%) [10].

4.4 Coalescence Enhancement Technologies

4.4.1 Passive Coalescence (Design-Based)

Baffle placement optimization: From Khan et al. (2022) CFD studies

Single baffle at depth 0.5 m in 0.87 m settler: - Disrupts channeling flow (positive effect) - Creates low-velocity eddy zone (coalescence region) - Reduces settling time by 25-30% - Cu loss reduction: 37% improvement documented

Multiple-baffle configurations: Generally less effective than single baffle due to flow misdirection and dead zones.

Optimal settler modifications: - Single baffle: 40-60% depth - Expanded settlement zone: 3.5:1 length-to-width ratio - Sloped bottom: Promotes consolidation of settled matte

4.4.2 Active Coalescence (Operational Control)

Electromagnetic stirring: Rahman et al. (2025) preliminary study - Applied EM field: 2-5 Tesla - Matte droplet velocity increase: 2-3× - Interfacial drag increase promotes coalescence

Acoustic enhancement: (Emerging technology, limited literature) - Ultrasonic frequency: 20-40 kHz - Cavitation bubbles promote droplet merging - Pilot-scale studies show promise; industrial validation pending

4.5 Residual Copper Losses and Entrainment

4.5.1 Critical Droplet Size Analysis

Droplets below critical size Φ_c cannot settle due to surface tension forces:

$$\mathbf{\Phi c} = \frac{\sigma \cdot cos\theta}{pgh}$$

With typical values: σ ≈ 0.4 N/m (slag-matte interfacial tension, high-FeO slag) - cos θ ≈ -0.17 (non-wetting; θ ≈ 100°) - ρ ≈ 3100 kg/m^3 - g = 9.81 m/s^2 - h = 0.5-1.0 m (settler column height)

Calculated: Φ_c ≈ 8-16 μm

Physical meaning: Approximately 30-40% of matte droplets formed during smelting are smaller than this critical size and cannot settle through gravity alone, regardless of slag composition or time [11]

This explains why: 1. Industrial slag cleaning cannot achieve <0.5 wt% residual Cu 2. Coalescence enhancement becomes critical for Cu recovery improvement 3. Vacuum or pressure-driven separation technologies are being explored

4.6 Thermodynamic vs. Kinetic Control

4.6.1 Temperature Optimization Paradox

Temperature increases both favoring and inhibiting effects:

Favorable effects (higher T): - Lower slag viscosity: ↓ μ by ~2% per °C increase - Increased settling velocity: ↑ v_s by ~2.5% per °C - Enhanced coalescence: Ea reduced at higher T - Faster chemical reactions in slag

Inhibiting effects (higher T): - Increased copper partitioning to slag: ↑ [Cu]_slag by thermodynamic equilibrium shift - Enhanced matte entrainment via flotation - Increased volatilization of zinc/lead - Higher capital and operating costs - Accelerated refractory erosion

Optimal resolution: Operate at 1350-1400°C to maximize settling velocity while minimizing thermodynamic Cu partition into slag. Above 1400°C, entrainment and thermodynamic losses outweigh kinetic benefits [12].

4.7 Future Research Priorities

4.7.1 Gaps in Current Knowledge

1. **Foaming slag dynamics:** Only 1 paper (Shimasaki et al., 2024) addresses gas bubble effects on settling. Industrial furnaces regularly operate with foam; mechanisms underdeveloped.
2. **Non-Newtonian slag behavior:** Most models assume Newtonian viscosity. Real slags show non-Newtonian shear-thinning; impact on settling not quantified.
3. **Three-phase settling:** Industrial slags contain solid phases (magnetite, olivine). Ternary system kinetics underexplored.
4. **Pressure effects:** Limited data on how 1-5 bar pressure affects settling kinetics in pressure-smelting designs.
5. **Transient phenomena:** Models assume steady-state; furnace operations are transient (batch cycles, varying feed rates).

5. CONCLUSIONS

5.1 Primary Findings

1. **Stokes' law governs:** Particle settling velocity is inversely proportional to slag viscosity and directly proportional to particle size squared: (v_s d^2/)
2. **Slag viscosity is critical parameter:**
    - Minimum viscosity at basicity C/S = 1.3
    - Reducing viscosity by one-third decreases copper losses by 37%
    - Temperature control (1350-1400°C) achieves 2-3× settling acceleration
3. **Particle size distribution dominates:**
    - Settling time increases as d^{-2}; droplets <20 μm cannot settle
    - Coalescence enhancement critical to concentrate droplets
    - 50-100 μm optimal particle size for industrial settling
4. **Composition optimization:**
    - Optimal slag: CaO 40-45%, SiO_2 30-35%, Al_2O_3 12-16%, MgO 5-8%, FeO 2-5%
    - Basicity = 1.3 ± 0.10
    - FeO content management critical (each 1% excess increases settling time ~5%)

5. **Industrial residence time:** 4-5 hours standard for achieving 90-95% matte-slag separation

5.2 Quantitative Summaries

Settling velocity equation (practical use):

$$\mathbf{vs[m/s] = 2.31\ x\ 10^{-5}\ x\ \frac{d^2[\mu m^2]}{\mu[Pa\ x\ S]}}$$

Settling time (0.5 m column):

$$\mathbf{T_{[hours]} = \frac{0{,}604\ x\ \mu[Pa\ x\ s]}{d^2[\mu m^2]}}$$

Slag viscosity temperature dependence:

$$\mathbf{d^2[\mu m^2] = 0{,}002\ x\ exp\ (\frac{2{,}3\ x\ 10^5}{T[K]})}$$

5.3 Industrial Recommendations

1. **Composition control:** Maintain slag basicity $CaO/SiO_2 = 1.30 \pm 0.05$ via automated XRF analysis and flux adjustments
2. **Temperature management:** Target 1350-1400°C balance of kinetics vs. thermodynamics
3. **Magnetite reduction:** Implement slag cleaning with reductant addition to reduce FeO to <5 wt%
4. **Settler design:** Employ single baffle at 45-55% settler depth; avoid multiple baffles
5. **Coalescence enhancement:** Consider design modifications or active mixing for 30-40% efficiency improvement
6. **Monitoring:** Real-time slag composition and temperature monitoring with feedback control loops

5.4 Future Directions

1. **Advanced characterization:** In-situ observation of droplet settling in industrial furnaces (high-temperature visualization technology)
2. **Non-Newtonian modeling:** Develop shear-rate-dependent viscosity models for real slag systems
3. **Pressure operation:** Quantify settling kinetics in 1-5 bar pressure systems
4. **Machine learning:** Develop predictive models for optimal slag composition based on operating parameters
5. **Alternative technologies:** Evaluate pressure-driven, electromagnetic, or ultrasonic-enhanced settling

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