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Ferrous-Assisted Carbonation Mud Dosing Improves Activated-Sludge Settleability

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Abstract

Background: Secondary clarifier limitations and poor sludge settleability often constrain the performance of conventional activated sludge (CAS) under stringent effluent limits. Valorizing carbonation mud (CM), a $CaCO_3$-rich by-product from sugar manufacture, as an alkalinity source and ballast, particularly when paired with ferrous sulfate ($FeSO_4$), could improve settleability without pH excursions.

Methods: A tiered program combined jar tests with a continuous bench-scale ASP design. Jar tests quantified settling volume (mL L^{-1}) under fixed mixing (rapid 120 rpm, 60 s; slow 20 rpm, 5 min) across $FeSO_4$ (0–80 mg L^{-1} for co-dosing; 0–400 mg L^{-1} Fe-only) and CM (0–720 mg L^{-1}), with pH and temperature held near 7.5–7.6 and 14–15 °C. Hydrodynamic effects were resolved by varying slow-mix speed (10–25 rpm) and contact time (2–20 min). Cross-run synthesis reported percent reductions versus paired controls and identified operating windows.

Results: Co-dosing reduced settling volume by 10.3–16.5% (minimum 810 mL L^{-1} at 80/720 mg L^{-1} $FeSO_4$/CM). Lowering the slow-mix speed from 20 to 10 rpm yielded a 7.1% decrease, and extending the contact time from 2 to 20 minutes delivered a monotonic 20.2% decrease. A broad co-variation window, $FeSO_4$ 50–80 mg L^{-1} with CM 350–320 mg L^{-1}, consistently achieved 730–740 mL L^{-1} (minimum 730 mL L^{-1}). $FeSO_4$-only dosing produced the most significant single-factor reduction (−25%) with a plateau near 350–400 mg L^{-1}. Across all conditions, pH remained neutral to slightly alkaline.

Conclusions: Moderate $FeSO_4$ with CM ballast, applied under gentle, prolonged mixing, substantially improves settleability while maintaining neutral pH. The practical window ($FeSO_4$ 40–70 mg L^{-1} with CM 320–360 mg L^{-1}, or $FeSO_4$ ≥350 mg L^{-1} alone; slow mix 10 rpm for ≥15–20 min) is operationally attainable and motivates continuous-pilot validation with COD–N–P and SVI endpoints alongside routine metals/leachate compliance.

Keywords: Activated sludge; Carbonation mud; Ferrous sulfate; Settleability (SVI); Ballasted bioflocculation

1. INTRODUCTION

Municipal wastewater treatment plants (WWTPs) are increasingly facing concurrent pressures to comply with stringent effluent standards for carbon, nitrogen, and phosphorus while operating with aging infrastructure and constrained operating budgets. Within conventional activated sludge processes (ASP), plant bottlenecks frequently center on secondary clarifier performance and sludge settleability, where episodes of high sludge volume index (SVI) and bulking/foaming can compromise solids capture, upset nitrification, and drive total suspended solids (TSS) excursions [1-3]. Improving settleability without undermining biological conversions remains a persistent challenge, particularly under diurnal loading, low temperatures, and variable influent composition typical of municipal systems.

A complementary strategy to process control and configuration is the targeted use of chemical or mineral additives to enhance floc formation, ballast solids, and stabilize pH/alkalinity. Iron salts ($FeSO_4$, $FeCl_3$) are widely applied to promote coagulation/bridging and to capture soluble phosphorus, while alkaline reagents (lime, soda ash) provide buffering to sustain nitrification; both approaches, however, can introduce trade-offs in cost, corrosion/scaling, or pH overshoot [4-6]. At the same time, circular-economy pathways motivate valorization of low-cost industrial by-products as functional additives in WWTPs. One such by-product is carbonation mud (CM) from the sugar industry, a $CaCO_3$-rich slurry collected from carbonation lines or legacy ponds. CM is abundant near sugar factories, contains significant alkalinity (as $CaCO_3$), and carries trace micronutrients that may serve as co-factors for microbial metabolism [7-9].

From a mechanistic standpoint, CM could influence ASP performance through at least three routes: (i) alkalinity supply to buffer nitrification demand (~7.1 mg as $CaCO_3$ per mg NH_4–N oxidized), stabilizing process pH in the neutral-to-slightly alkaline range; (ii) ballasting/adsorptive templating, where $CaCO_3$ particles provide surface area for capture of colloids and extracellular polymeric substances (EPS), promoting denser floc packing; and (iii) micronutrient supplementation (Ca, Mg, Fe, Mn, Zn, Cu) for enzymatic activity and floc integrity [10, 11]. When paired with a coagulant such as $FeSO_4$, additional benefits are expected through charge neutralization and inter-particle bridging, potentially improving settleability and nutrient removal without requiring extreme pH manipulation [12, 13].

Despite these plausible advantages, systematic evaluation of CM as an ASP additive remains limited. Prior studies on ballasted flocculation (microsand, GAC fines) and iron-assisted coagulation in biological systems suggest that gentle, prolonged mixing is crucial for building a floc structure while avoiding shear-induced breakage [14-16]. However, there is a lack of integrated studies that concurrently interrogate (a) additive chemistry (CM alone vs. $FeSO_4$ vs. co-dosing), (b) hydrodynamics (rapid/slow mixing intensity and contact time), and (c) operational stability (pH/alkalinity and temperature) under conditions relevant to municipal ASPs.

This work addresses that gap by combining tiered jar tests with a continuous bench-scale ASP pilot to interrogate the performance, stability, and practicality of dosing CM, with and without $FeSO_4$. The jar tests screen dose ranges and hydrodynamic settings to map the settling response of activated-sludge mixed liquor, while the pilot (control vs. CM-dosed) evaluates primary outcomes, effluent COD, TKN/NH_4–N/NO_3–N, TP/PO_4–P, pH/alkalinity stability, and sludge settleability (SVI), along with secondary outcomes (MLSS/MLVSS dynamics, observed sludge yield, dewaterability surrogates, and techno-economic indicators). We hypothesize that appropriately dosed CM will (i) enhance COD–N–P removals and (ii) reduce SVI relative to controls, via the combined effects of alkalinity buffering, micro-ballasting/adsorption, and iron-mediated flocculation, without introducing contaminants above regulatory thresholds.

The paper is organized as follows. Section 2 details materials, characterization of CM, experimental systems, operating conditions, and statistical/QA procedures. Section 3 presents jar-test and pilot results, emphasizing the roles of chemistry and hydrodynamics, and synthesizes a practical operating window for co-dosing. Section 4 discusses mechanistic implications, limitations, and scale-up guidance, including environmental, health, and safety (EHS) considerations for CM handling and metals/leachate compliance.

2. MATERIALS AND METHODS

2.1 Study Design and Overview

This study evaluates the performance, stability, and practicality of dosing sugar-industry carbonation mud (CM) into the Activated Sludge Process (ASP) to enhance removal of organics and nutrients and to improve sludge settleability. The work proceeds in two experimental tiers: (i) jar tests to screen dose ranges and settling effects, followed by (ii) a continuous bench-scale ASP pilot (control vs CM-dosed) operated under representative municipal conditions. Primary outcomes are effluent quality (COD, TKN/NH_4–N/NO_3–N, TP/PO_4–P), pH/alkalinity stability, and sludge settleability (SVI). Secondary outcomes include MLSS/MLVSS dynamics, observed sludge yield and dewaterability surrogates, and techno-economic metrics.

Rationale: Carbonation mud is a $CaCO_3$-rich by-product that can (i) supply alkalinity for pH control, (ii) provide trace micronutrients essential to microbial metabolism, and (iii) aid coagulation/adsorption and mass transfer in mixed liquor. The hypothesis is that appropriately dosed CM will increase COD–N–P removals and reduce SVI without introducing contaminants above regulatory limits.

2.2 Materials

2.2.1 Carbonation Mud (CM): Source, Preparation, and Characterization

- **Source and collection:** CM is obtained from the adjacent sugar factory carbonation line or legacy storage ponds. Composite samples are collected from ≥5 points and homogenized.
- **Pre-processing:** Air-dry at 40–50 °C to constant mass, gently disaggregate, and sieve to <250 µm for jar tests and to <500 µm for pilot dosing; store as a slurry (10–20 % w/w) in a sealed, mixed tank.
- **Physical/chemical properties:**
    - **Moisture and density:** oven moisture; slurry density by pycnometer.
    - **Alkalinity (as $CaCO_3$):** strong-acid titration to pH 4.5; report as mg $CaCO_3$ g^{-1} dry CM.
    - **Mineralogy & particle size:** XRD (for $CaCO_3$ polymorphs and impurities), laser diffraction ($d_{10}/d_{50}/d_{90}$).
    - **Elemental composition:** ICP-OES/ICP-MS on acid digest for macro/micronutrients (Ca, Mg, K, Na, Fe, Mn, Zn, Cu, etc.).
    - **Leachable metals & anions:** standardized leaching test (TCLP/EN-12457) to benchmark against applicable sludge-use/landfill criteria.
    - **pH and conductivity:** slurry measurements at 25 °C.

2.2.2 Wastewater and Inoculum

- **Wastewater matrix:** Primary influent from a municipal WWTP (or a synthetic matrix prepared to match COD/N/P and alkalinity). Record influent variability per sampling day.
- **Seed sludge (inoculum):** Return activated sludge (RAS) from the same WWTP, screened (2 mm), acclimated during start-up.

2.2.3 Reagents and Standards

Analytical-grade reagents and certified standards are used for all determinations. Methods follow APHA Standard Methods (latest edition) or equivalent ISO procedures; specific method numbers will be reported alongside each analyte in the final manuscript/SI.

2.3 Experimental Systems

2.3.1 Jar-Test Apparatus

A six-place programmable jar tester (independent paddle rpm) equipped with graduated 1 L beakers is used for rapid/slow mixing and settling observations (representative photo in proposal figures). Temperature is maintained at 20 ± 2 °C.

2.3.2 Continuous Bench-Scale ASP Pilot

- **Configuration:** Modular glass/plexiglass system comprising selector (optional), anoxic zone, aeration tank, and secondary clarifier with RAS/WAS loops. Control and CM-dosed trains operate in parallel when resources allow; otherwise conditions are alternated in a cross-over schedule.
- **Volumes and hydraulics:** Working volumes are sized to provide municipal ranges of HRT and SRT (see Operating Conditions). Feed equalization tank (50–100 L) ensures steady influent.
- **Aeration and mixing:** Fine-bubble diffusers in the aerobic tank; mechanical mixers in equalization/anoxic tanks. DO setpoint: 1.8–2.5 mg L^{-1} (PID-controlled).
- **Instrumentation:** Online pH and DO (daily calibration), temperature, and flow meters; manual sampling ports at influent, anoxic, aerobic, and clarifier effluent.

- **Dosing system:** CM slurry tank (~100 L) with overhead mixer; peristaltic metering pumps deliver controlled doses to selected points (influent, selector/anoxic, or aeration).

2.4 Experimental Design and Operating Conditions

2.4.1 Commissioning and Baseline

1. System assembly & leak testing.
2. **Inoculation and acclimation:** Start with MLSS ≈ 2.0–2.5 g L^{-1}; ramp aeration to maintain DO setpoint; operate without CM until steady effluent is reached (baseline ≥10 system HRTs).

2.4.2 Operating Conditions (target ranges)

- **Temperature:** ambient lab (20–25 °C); record continuously.
- **Hydraulic Retention Time (HRT):** 8–12 h (tuned within design ranges referenced in the proposal's Table 1-2).
- **Sludge Retention Time (SRT):** 10–15 d (controlled via WAS rate; verified from mass balance).
- **MLSS/MLVSS:** maintain 2.0–3.5 g L^{-1} / 1.4–2.8 g L^{-1}.
- **F/M:** 0.1–0.3 kg BOD_5 kg^{-1} MLVSS d^{-1} (estimated from influent loading).
- **DO:** 1.8–2.5 mg L^{-1} in the aeration tank.
- **pH:** 6.8–7.6 (monitored; CM expected to buffer to the upper range).

These baselines ensure nitrification capacity; ranges may be tuned during operation to maintain steady state.

2.4.3 CM Dosing Strategy

- **Dose levels:** Four levels are planned: 0, 50, 100, 200 mg L^{-1} as $CaCO_3$-equivalent alkalinity (exact levels may be refined from jar-test results).
- **Point of addition:** Tested at (i) influent/equalization, (ii) selector/anoxic, and (iii) aeration tank.
- **Exposure schedule:** Each dose–location condition runs for ≥7 consecutive days after a 3–5 day transition, in randomized order to mitigate drift. A zero-dose control is repeated periodically to detect temporal bias.
- **Process control:** WAS and aeration are adjusted to hold SRT and DO within target bands across conditions.

2.4.4 Jar-Test Protocol (screening and support to pilot)

- **Matrix:** equalized influent or mixed liquor.
- **Sequence:** Rapid mix (G≈700–900 s^{-1}, 1 min) → Slow mix (G≈30–50 s^{-1}, 5–10 min) → 20 min quiescent settling.
- **Doses:** 0, 25, 50, 100, 200, 400 mg L^{-1} (as $CaCO_3$-eq).
- **Measurements:** supernatant turbidity, pH/alkalinity shift, settled sludge volume, SVI (mL g^{-1}) using MLSS from a parallel sample.
- **Outcome:** select dose range producing maximal SVI reduction with minimal excess alkalinity or turbidity.

2.5 Sampling and Analytical Methods

2.5.1 Frequency and Locations

- **Daily:** influent and effluent COD, NH_4–N, NO_3–N, PO_4–P, pH, alkalinity, temperature.

- **3×/week:** TKN (or TN), TP, TSS/MLSS/MLVSS, SVI (clarifier mixed liquor), DO profile.
- **Weekly:** sludge dewaterability surrogate (capillary suction time, CST), metal scans (ICP) on CM and wasted sludge during representative conditions.

2.5.2 Methods (standards and QA)

- Analyses follow APHA Standard Methods/ISO (latest edition) for COD, BOD_5 (optional), TKN/NH_4–N/NO_3–N, TP/PO_4–P, TSS/MLSS/MLVSS, alkalinity, and SVI.
- **QC/QA:** instrument calibration each run; method blanks, field/lab duplicates (10 %); matrix spikes for colorimetric assays; certified standards for ICP; control charts for key analytes.
- **Sample handling:** chain-of-custody forms; preservation and holding times per method.

2.5.3 Calculations and Derived Metrics

- **Removal efficiency (%):** $\eta = 100(1 - C_{\mathrm{eff}}/C_{\mathrm{inf}})$for each analyte.
- **F/M ratio:** $F/M = \frac{QS_0}{VX}$ with S_0 as influent BOD_5 (or COD-equivalent if justified), X as MLVSS.
- **Observed sludge yield:** $Y_{\mathrm{obs}} = \frac{\text{WAS TSS production (kg d}^{-1})}{\text{COD removed (kg d}^{-1})}$.
- **SVI (mL g^{-1}):** settled sludge volume after 30 min / MLSS (g L^{-1}).
- **Alkalinity balance (design aid):** nitrification consumes alkalinity (~7.1 mg as $CaCO_3$ per mg NH_4–N oxidized); CM contribution is accounted as $CaCO_3$-equivalent from titration.

2.6 Statistical Analysis

- **Design:** Factorial scheme with factors Dose (4 levels) and Addition Point (3 levels); repeated measures across time.
- **Primary endpoints:** Effluent COD, NH_4–N, PO_4–P, and SVI.
- **Models:** Linear mixed-effects models with fixed effects for Dose, Addition Point, and their interaction; Reactor/Day as random effects. Assumptions checked via residual diagnostics; Box-Cox transformation applied as needed.
- **Contrasts and multiplicity:** Pre-specified contrasts compare each dose to control and the best-performing addition point; p-values adjusted (Holm). Report effect sizes (mean differences or ratios) with 95 % CIs.
- **Sensitivity analyses:** Robust regression; exclusion of transient days after condition switches; alternative covariance structures.
- **Software:** R (v4.x) with documented packages.

2.7 Techno-Economic Assessment (screening level)

- **Cost items:** (i) CM handling and dosing (collection, transport, slurry prep, pumping), (ii) avoided chemical costs (alkalinity agents, micronutrient salts, coagulants/polymers), (iii) energy impacts (aeration/mixing), and (iv) sludge handling/disposal savings (via SVI/Y_{obs} reductions).
- **Normalization:** Reported as cost per m^3 treated and per kg COD (or TN/TP) removed.
- **Scenario analysis:** Near-factory WWTP vs non-proximate WWTP; sensitivity to CM moisture and metal compliance.

2.8 Environmental, Health, and Safety (EHS)

- CM storage in closed, labeled tanks; secondary containment; routine dust control during dry handling.

- Leachate/metals tracked to ensure effluent and biosolids remain within regulatory thresholds.
- Waste from analyses is managed per institutional hazardous-waste procedures.

3. RESULTS

3.1 Jar-test overview and environmental conditions

Jar tests were conducted to quantify how additive chemistry, carbonation mud (CM), ferrous sulfate ($FeSO_4$), and mixing hydrodynamics affect the settleability of activated-sludge mixed liquor, measured as settling volume ($mL·L^{-1}$) after quiescent settling. Across all runs, temperature was stable at ~14–15 °C and pH remained neutral to slightly alkaline (≈7.5–7.6), minimizing thermal or extreme-pH confounding.

3.2 Dose–response under fixed mixing

Under fixed mixing (rapid 120 rpm for 60 s; slow 20 rpm for 5 min), co-dosing $FeSO_4$ and CM progressively reduced settling volume relative to the no-additive control. In the first series, increasing $FeSO_4$ from 20 to 60 mg alongside CM from 180 to 540 mg decreased the settling volume from 970 mL/L (control) to 870 mL/L $·L^{-1}$, a 10.3% improvement (Table 1).

As shown in Figure 1, co-dosing $FeSO_4$–CM under fixed mixing (rapid 120 rpm, 60 s; slow 20 rpm, 5 min) lowered the settling volume from the paired control (970 mL L^{-1}) to as low as 810 mL L^{-1} at 80/720 mg L^{-1}. The two series exhibit consistent trends, with progressive improvements across 20/180→60/540 mg L^{-1} in Series 1 and a minimum at 80/720 mg L^{-1} in Series 2; the pH remained ≈approximately 7.5–7.6.

Extending the dose range ($FeSO_4$ 40–80 mg; CM 360–720 mg) lowered the minimum to 810 $mL·L^{-1}$ at 80/720, amounting to a 16.5% reduction versus the series control (Table 2). pH stayed near 7.5–7.6 throughout (Tables 1–2).

Table 1. Jar-test screening of carbonation-mud (CM) and ferrous sulfate doses under fixed mixing conditions

Sample ID	Ferrous sulfate dose (mg)	Carbonation mud dose (mg)	Rapid mix speed (rpm)	Rapid mix time (s)	Slow mix speed (rpm)	Slow mix time (min)	Settling volume (mL/L)	pH	Temperature (°C)
Control	0	0	120	60	20	5	970	7.57	15.4
1	20	180	120	60	20	5	910	7.55	14.9
2	30	270	120	60	20	5	930	7.56	14.6
3	40	360	120	60	20	5	890	7.53	14.6
4	50	450	120	60	20	5	880	7.52	14.7
5	60	540	120	60	20	5	870	7.51	14.8

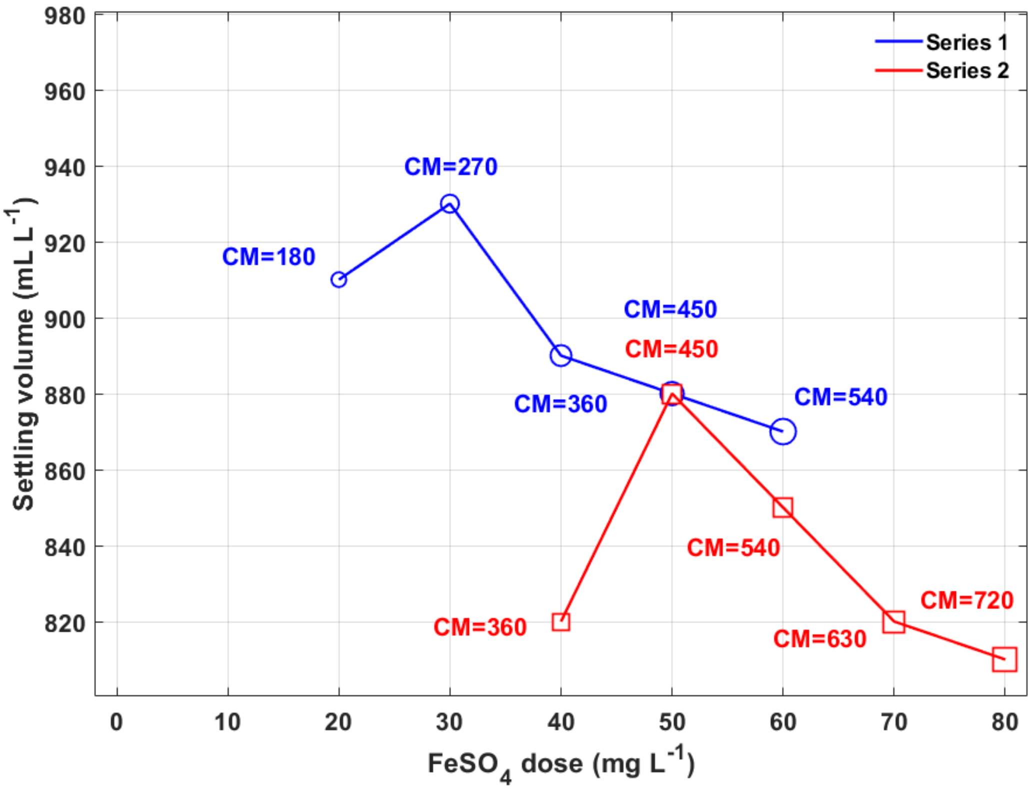

Figure 1. Co-dosing $FeSO_4$–CM under fixed mixing reduces settling to 810 mL L^{-1}; two screening series show consistent trends.

Table 2. Jar-test screening (higher dose series) under fixed mixing conditions

Sample ID	Ferrous sulfate dose (mg)	Carbonation mud dose (mg)	Rapid mix speed (rpm)	Rapid mix time (s)	Slow mix speed (rpm)	Slow mix time (min)	Settling volume (mL/L)	pH	Temperature (°C)
Control	0	0	120	60	20	5	970	7.58	15.3
1	40	360	120	60	20	5	820	7.54	14.8
2	50	450	120	60	20	5	880	7.55	14.7
3	60	540	120	60	20	5	850	7.52	14.6
4	70	630	120	60	20	5	820	7.53	14.8
5	80	720	120	60	20	5	810	7.52	14.6

3.3 Hydrodynamics at fixed dosing: slow-mix speed and time

At fixed dosing ($FeSO_4$ 40 mg; CM 360 mg; rapid 120 rpm, 60 s), changing slow-mix speed and time yielded clear trends. Reducing slow-mix speed from 20 to 10 rpm (5 min) improved compaction from 990 to 920 mL·L^{-1} (−7.1%), while higher speeds (≥15 rpm) produced larger volumes (960–935 mL·L^{-1}), indicating shear sensitivity (Table 3).

As shown in Figure 2, at fixed dosing ($FeSO_4$ 40 mg L^{-1}; CM 360 mg L^{-1}) and a 5-min slow-mix period, reducing slow-mix speed from 20→10 rpm decreased settling volume from 990→920 mL L^{-1} (−7.1 %). In contrast, higher speeds (≥15 rpm) yielded larger volumes (960–935 mL L^{-1}), consistent with shear sensitivity (Table 3).

Holding speed at 10 rpm and extending the slow-mix time from 2 to 20 min reduced the settling volume monotonically (990→950→880→810→790 mL/L), with the most prolonged contact achieving a 20.2% improvement over the 2-min condition (Table 4).

As shown in Figure 3, at fixed dosing ($FeSO_4$ 40 mg L^{-1}; CM 360 mg L^{-1}) and a slow-mix speed of 10 rpm, extending the slow-mix contact time from 2 to 20 min reduced the settling volume from 990 to 790 mL L^{-1}. The most favorable range was 15–20 min, delivering an 18.2–20.2% improvement compared to the 2-min condition; pH and temperature remained stable (≈7.58–7.60; 13.9–14.1 °C; Table 4).

Table 3. Effect of slow-mix speed at fixed dosing

Sample ID	Ferrous sulfate dose (mg)	Carbonation mud dose (mg)	Rapid mix speed (rpm)	Rapid mix time (s)	Slow mix speed (rpm)	Slow mix time (min)	Settling volume (mL/L)	pH	Temperature (°C)
Control	40	360	120	60	20	5	990	7.62	14.3
1	40	360	120	60	10	5	920	7.57	14.2
2	40	360	120	60	15	5	960	7.60	13.9
3	40	360	120	60	20	5	930	7.60	13.8
4	40	360	120	60	25	5	935	7.60	13.9

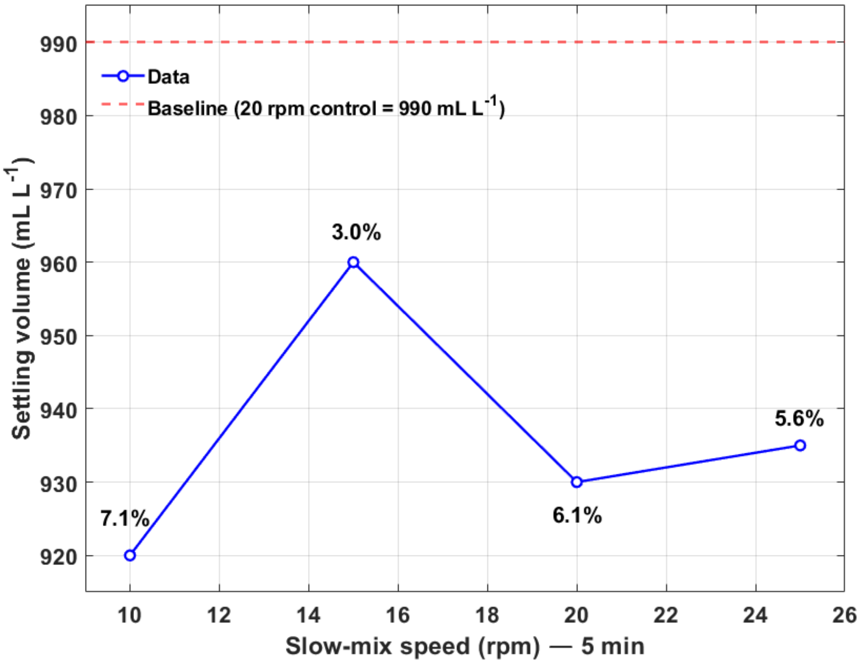

Figure 2. Slow-mix speed effect at fixed dose: 10 rpm minimizes settling volume (920 mL L^{-1}) vs 20 rpm baseline (990 mL L^{-1}).

Table 4. Effect of slow-mix time at fixed doses and slow-mix speed

Sample ID	Ferrous sulfate dose (mg)	Carbonation mud dose (mg)	Rapid mix speed (rpm)	Rapid mix time (s)	Slow mix speed (rpm)	Slow mix time (min)	Settling volume (mL/L)	pH	Temperature (°C)
1	40	360	120	90	10	2	990	7.58	14.1
2	40	360	120	90	10	5	950	7.58	14.0
3	40	360	120	90	10	10	880	7.59	13.9
4	40	360	120	90	10	15	810	7.60	14.0
5	40	360	120	90	10	20	790	7.60	13.9

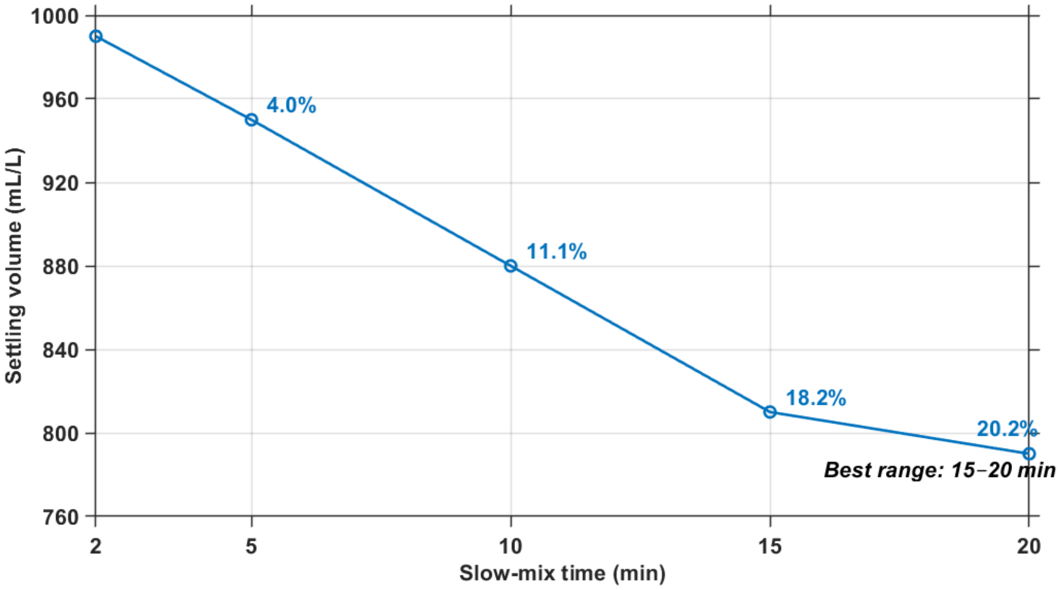

Figure 3. Slow-mix time effect (10 rpm): 2→20 min lowers settling to 790 mL L⁻¹; best range 15–20 min.

3.4 Additive formulation comparison

With mixing fixed (rapid 120 rpm, 90 s; slow 10 rpm, 20 min), formulation significantly influenced the outcomes. CM-only (400 mg) resulted in 800 mL·L⁻¹ (pH ≈7.6); a formulation annotated lime only (no $FeSO_4$; pH 8.38) yielded the same value (800 mL·L⁻¹), implying that elevating pH above neutrality alone did not further compact the sludge.

As shown in Figure 4, the formulation, under fixed mixing conditions (rapid: 120 rpm, 90 s; slow: 10 rpm, 20 min), strongly modulated settleability. CM-only (400 mg L⁻¹) and lime-only (no $FeSO_4$; pH=8.38) both yielded 800 mL L⁻¹, indicating that pH elevation alone did not further compact the sludge. Co-dosing $FeSO_4$ 40 mg L⁻¹ + CM 360 mg L⁻¹ achieved the lowest value (780 mL L⁻¹, −4.9% vs the run control 820 mL L⁻¹).

Co-dosing $FeSO_4$ 40 mg + CM 360 mg produced the best response, 780 mL·L⁻¹, a 4.9% reduction relative to that run's control (820 mL·L⁻¹) (Table 5).

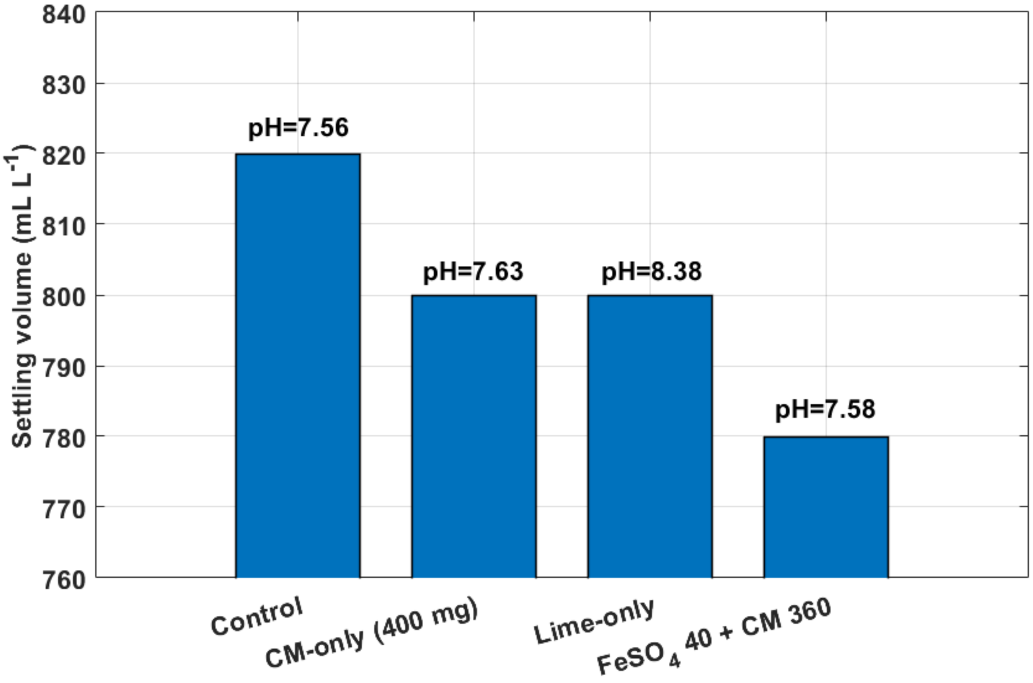

Figure 4. Formulation effects: $FeSO_4$+CM outperforms CM-only and lime-only (780 vs 800 mL L^{-1}) under fixed mixing.

Table 5. Effect of additive formulation at fixed mixing

Sample ID	Ferrous sulfate dose (mg)	Carbonation mud (CM) dose (mg)	Rapid mix speed (rpm)	Rapid mix time (s)	Slow mix speed (rpm)	Slow mix time (min)	Settling volume (mL/L)	pH	Temperature (°C)	Notes
Control	0	0	120	90	10	20	820	7.56	14.7	—
1	0	400	120	90	10	20	800	7.63	14.6	—
2	0	400	120	90	10	20	800	8.38	14.7	*Lime only*
3	20	380	120	90	10	20	790	7.58	15.1	—
4	40	360	120	90	10	20	780	7.58	15.3	—

3.5 Ferrous-sulfate–only series

As shown in Figure 5, increasing the $FeSO_4$ dose under fixed mixing (120 rpm, 60 s; 10 rpm, 20 min) produced a substantial monotonic reduction in settling volume from 960 to 720 mL L^{-1}. The response plateaued at ≈350–400 mg L^{-1}, and the two independent runs overlapped closely, indicating good repeatability.

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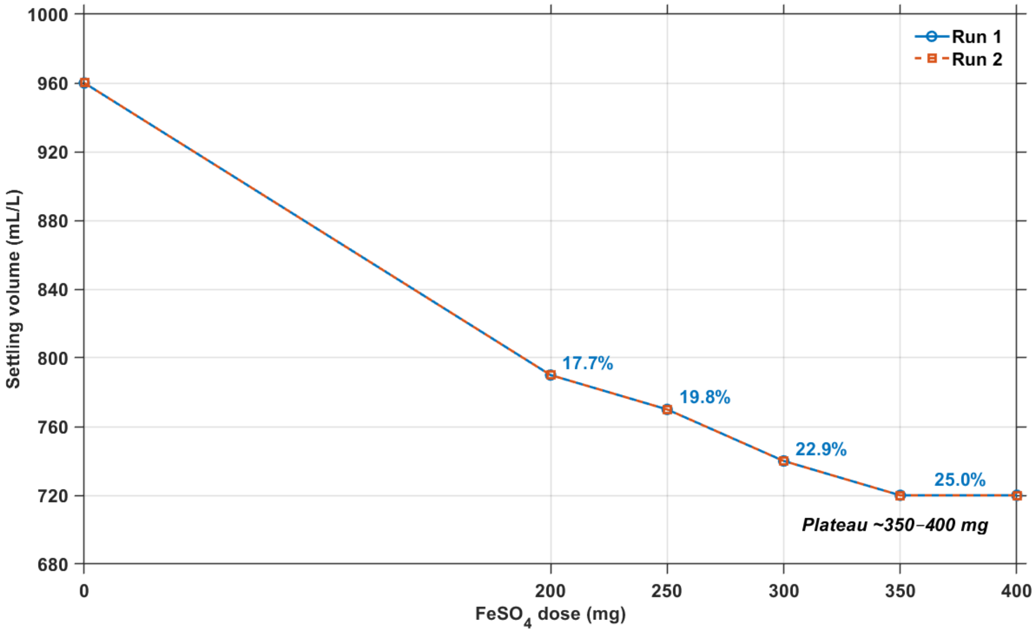

Figure 5. $FeSO_4$-only dose–response: settling volume drops to 720 mL L^{-1} with a plateau at ~350–400 mg L^{-1}; two runs overlap.

In the absence of CM (rapid 120 rpm, 60 s; slow 10 rpm, 20 min), increasing $FeSO_4$ produced a strong, monotonic dose–response: settling volume declined from 960 (control) to 720 mL·L^{-1} at 350–400 mg, a 25.0% improvement with a plateau beyond ~350 mg. An alternate run reproduced the same pattern, supporting repeatability (Tables 6–7). pH remained within 7.48–7.65 and temperature within 14.3–15.2 °C (Tables 6–7).

Table 6. Effect of ferrous sulfate dose at fixed mixing and no carbonation mud

Sample ID	Ferrous sulfate dose (mg)	Carbonation mud dose (mg)	Rapid mix speed (rpm)	Rapid mix time (s)	Slow mix speed (rpm)	Slow mix time (min)	Settling volume (mL/L)	pH	Temperature (°C)
Control	0	0	120	60	10	20	960	7.48	15.2
1	200	0	120	60	10	20	790	7.60	14.5
2	250	0	120	60	10	20	770	7.62	14.3
3	300	0	120	60	10	20	740	7.63	14.4
4	350	0	120	60	10	20	720	7.61	14.6
5	400	0	120	60	10	20	720	7.65	14.5

Table 7. (Alternate run) Effect of ferrous sulfate dose at fixed mixing and no carbonation mud

Sample ID	Ferrous sulfate dose (mg)	Carbonation mud dose (mg)	Rapid mix speed (rpm)	Rapid mix time (s)	Slow mix speed (rpm)	Slow mix time (min)	Settling volume (mL/L)	pH	Temperature (°C)
Control	0	0	120	60	10	20	960	7.48	15.2
1	200	0	120	60	10	20	790	7.60	14.5

2	250	0	120	60	10	20	770	7.62	14.3
3	300	0	120	60	10	20	740	7.63	14.4
4	350	0	120	60	10	20	720	7.61	14.6
5	400	0	120	60	10	20	720	7.65	14.5

3.6 Co-variation of $FeSO_4$ and CM

Under fixed mixing (rapid 120 rpm, 60 s; slow 10 rpm, 20 min), increasing $FeSO_4$ (40→80 mg) while decreasing CM (360→320 mg) consistently generated low settling volumes within 730–740 mL·L⁻¹. The minimum (730 mL·L⁻¹) represents a 21.5% improvement relative to the run's control (930 mL·L⁻¹). The response surface remained relatively flat across 50–80 mg $FeSO_4$ paired with 350–320 mg CM, indicating a broad operating window (Table 8).

As summarized in Figure 6, under fixed mixing (120 rpm, 60 s; 10 rpm, 20 min), the response surface was relatively flat across $FeSO_4$ = 50–80 mg L^{-1} paired with CM = 350–320 mg L^{-1}, yielding settling volumes within 730–740 mL L^{-1} (minimum 730 mL L^{-1}). This corroborates the broad operating window identified from Table 8 and supports robustness to modest co-dose shifts.

Table 8. Co-variation of ferrous sulfate and carbonation mud under fixed mixing

Sample ID	Ferrous sulfate dose (mg)	Carbonation mud (CM) dose (mg)	Rapid mix speed (rpm)	Rapid mix time (s)	Slow mix speed (rpm)	Slow mix time (min)	Settling volume (mL/L)	pH	Temperature (°C)
Control	0	0	120	60	10	20	930	7.62	14.5
1	40	360	120	60	10	20	740	7.55	14.3
2	50	350	120	60	10	20	730	7.56	14.2
3	60	340	120	60	10	20	730	7.57	14.5
4	70	330	120	60	10	20	740	7.55	14.4
5	80	320	120	60	10	20	730	7.56	14.3

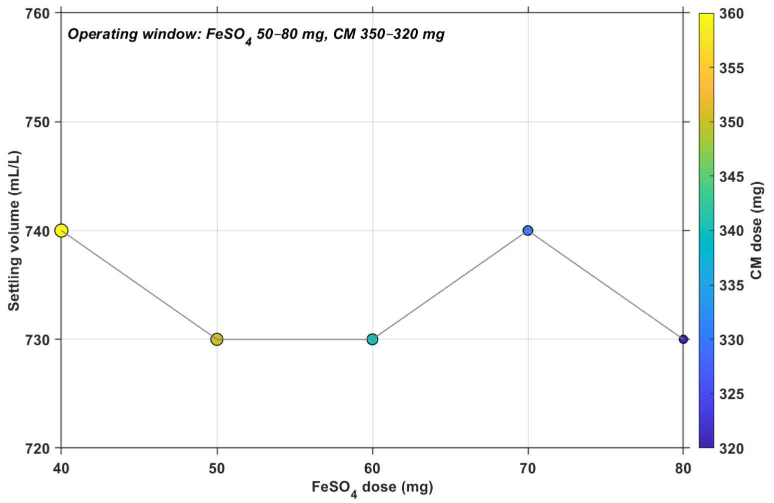

Figure 6. $FeSO_4$–CM co-dosing map: broad operating window ($FeSO_4$ 50–80; CM 350–320 mg L^{-1}) with minima ≈730 mL L^{-1}.

3.7 Cross-run synthesis and practical operating window

Because absolute controls varied by run (~820–990 mL·L⁻¹), effects were interpreted relative to paired controls. Across chemical and hydrodynamic factors, robust improvements of ~5–25% were observed (Tables 1–8). From a practical standpoint, a jar-test operating window emerges as: (i) $FeSO_4$ 40–70 mg with CM 320–360 mg (co-dose plateau), or (ii) $FeSO_4$ ≥350 mg alone where alkalinity supplementation is unnecessary; in both cases, slow-mix 10 rpm for ≥15–20 min with rapid 120 rpm for 60–90 s minimized settling volume without evidence of shear-induced dispersion (Tables 3–4, 8).

As summarized in Figure 7, cross-run improvements relative to paired controls span ~5–25% across factors. The $FeSO_4$-only series delivered the most significant reduction (25.0%, Tables 6–7), followed by co-variation $FeSO_4$–CM (21.5%, Table 8) and slow-mix time (20.2%, Table 4). Co-dosing under fixed mixing yielded 10.3–16.5% reductions (Tables 1–2), while changes in slow-mix speed and formulation alone produced more minor effects (7.1% and 4.9%, respectively).

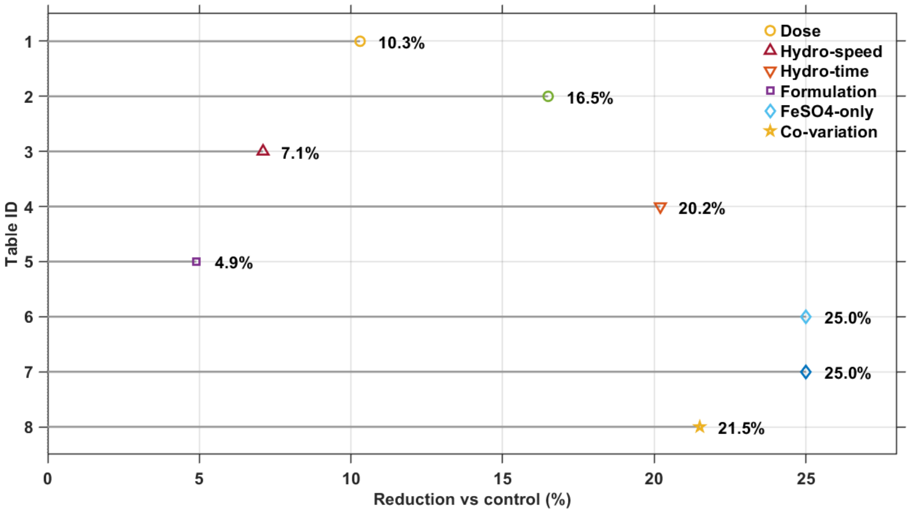

Figure 7. Cross-run percent reductions (vs control) by factor: maxima 25% ($FeSO_4$-only) and 21.5% (co-variation).

4. DISCUSSION

4.1 Principal findings and operational relevance

This study demonstrates that ferrous-assisted dosing of sugar-industry carbonation mud (CM) can measurably improve the settleability of activated-sludge mixed liquor under a range of mixing hydrodynamics, while maintaining a neutral to slightly alkaline pH and typical municipal temperatures. Across screening experiments, jar-settling volumes were reduced by ~5–25% relative to paired controls, with the most significant effects observed for $FeSO_4$-only (plateauing at ~350–400 mg L⁻¹) and for $FeSO_4$–CM co-variation windows that consistently achieved 730–740 mL L⁻¹ (minimum 730 mL L⁻¹). These outcomes translate into a practical operating window, where $FeSO_4$ is combined with CM at 320–360 mg L⁻¹ or $FeSO_4$ ≥350 mg L⁻¹ alone, together with low-shear, long-contact, slow mixing (10 rpm for ≥15–20 min). From a plant-operations perspective, this window is compatible with selector/anoxic contact times and does not require extreme pH manipulation, suggesting low retrofit complexity and modest OPEX.

4.2 Mechanistic interpretation

Three mutually reinforcing mechanisms likely underlie the observed benefits:

1. **Charge neutralization and inter-particle bridging by Fe(II/III) species:** Ferrous salts are well-known to promote coagulation and flocculation by compressing the electrical double layer and forming

hydroxide precipitates that bridge colloids [17-19]. The strong, monotonic $FeSO_4$-only response (25% reduction; plateau beyond ~350 mg L^{-1}) aligns with classical coagulant dose–response behavior where a critical coagulant demand is met and excess dosing yields diminishing returns [20].

2. **Ballasting, adsorption, and micro-aggregate templating by CM solids:** CM comprises $CaCO_3$-rich particles with micron-scale sizes that act as low-density ballast, providing additional surface area for the adsorption of soluble/colloidal organics, as well as extracellular polymeric substances (EPS), which facilitates denser floc packing during quiescent settling [4, 21]. The similarity of CM-only and lime-only outcomes (both 800 mL L^{-1}) despite distinct pH suggests that the solids-associated functions of CM are more influential than bulk pH elevation alone in these tests.
3. **Alkalinity buffering and micronutrient supply:** CM titration capacity (as $CaCO_3$) can offset nitrification-related alkalinity consumption (~7.1 mg $CaCO_3$ per mg NH_4–N oxidized) and stabilize pH in the upper-neutral range [6]. At the same time, trace metals (Fe, Mn, Zn) may serve as co-factors for microbial metabolism, supporting floc integrity and nitrifier resilience under load fluctuations [7]. The stable pH (≈7.5–7.6) and the absence of performance deterioration at higher $FeSO_4$/CM combinations are consistent with these buffering effects.

Notably, the lack of added benefit for lime-only relative to CM-only indicates that bulk pH shifts above neutrality are neither necessary nor sufficient to enhance compaction at the tested conditions. Instead, improvements arise when coagulation/bridging ($FeSO_4$) and ballasting/adsorptive templating (CM) are jointly available, consistent with the co-dosing plateau observed across $FeSO_4$ concentrations of 50–80 mg L^{-1} and CM concentrations of 350–320 mg L^{-1}.

4.3 Hydrodynamics as an enabling condition

Hydrodynamic control emerged as a coequal lever with chemistry. Two patterns are salient: (i) reducing slow-mix speed from 20→10 rpm decreased settling volume (−7.1%) and (ii) extending slow-mix time from 2→20 min delivered monotonic gains (up to −20.2%). These results are consistent with floc maturation kinetics where gentle, prolonged mixing favors contact, enmeshment, and EPS-mediated restructuring. At the same time, higher shear rates (>15 rpm here) promote floc erosion and re-entrainment [8, 9]. The operational translation is straightforward: provide a low-G contact zone, typically an anoxic selector or a dedicated flocculation compartment, targeting at least 15 minutes of gentle mixing before the secondary clarifier. This can often be achieved with existing mixers by setpoint adjustments rather than capital modifications.

4.4 Process implications for full-scale ASPs

Settleability and clarifier performance: Reductions of 150–240 mL L^{-1} in jar-settling volume (relative to controls) imply meaningful decreases in sludge blanket heights and improved solids flux margins in secondary clarifiers [10]. When translated to SVI via concurrent MLSS measurements (planned in the pilot), similar percentage reductions are anticipated, which can unlock higher RAS rates, stabilize nitrification under diurnal loading, and reduce effluent TSS carryover.

pH/alkalinity stability: The neutral to slightly alkaline pH across all runs suggests that CM can provide distributed alkalinity without the high-pH excursions observed with lime addition, thereby reducing the risks of ammonia toxicity to heterotrophs and nitrifiers. In plants constrained by alkalinity during winter nitrification, CM could displace part of the caustic/lime demand while simultaneously enhancing settling.

Chemical substitution and cost: In the co-dosing window, $FeSO_4$ requirements are modest (40–70 mg L^{-1}) compared with typical primary/tertiary coagulation regimes, and CM is a low- or no-cost by-product near sugar factories. A screening-level TEA should therefore consider avoided purchases of alkalinity agents and polymers, possible reductions in aeration energy due to improved oxygen transfer (via cleaner liquor) [11], and savings in sludge handling/disposal if SVI and observed yield (Yobs) decrease [12].

4.5 Comparison with prior work

The Fe-assisted improvement in settleability echoes reports where iron salts enhanced activated-sludge floc strength, dewaterability, and phosphorus capture without compromising nitrification at neutral pH [1, 3, 13]. The role of carbonate-rich media as ballast/adsorbent has been noted in bioflocculation and ballasted flocculation systems (microsand, GAC fines), which similarly rely on gentle mixing to promote contact and capture [4, 14]. Our findings contribute to this body of evidence by demonstrating that a waste $CaCO_3$ stream (CM) can serve as ballast and alkalinity source while avoiding the pH overshoot associated with lime, and offering a wider operating window when paired with $FeSO_4$.

4.6 Limitations and sources of uncertainty

Two methodological caveats should frame interpretation. First, jar tests were conducted at ~14–15 °C, whereas the Methods specified 20 ± 2 °C for the jar apparatus control. Although pH and temperature were stable within runs, absolute values could shift due to seasonal temperature and viscosity changes. Second, replicate numbers were limited for some conditions; while trends were robust and, for Fe-only, reproduced in an independent run, future work should include $n \geq 3$ replicates per condition with confidence intervals and mixed-effects modeling to quantify uncertainty and time effects.

4.7 Priority directions for pilot and scale-up

The bench-scale ASP pilot should test two implementation archetypes: (i) co-dosing $FeSO_4$ 50–60 mg L^{-1} with CM 340–360 mg L^{-1} dosed to the selector/anoxic zone to secure ≥15–20 min low-G contact; and (ii) Fe-only at ~350 mg L^{-1} where alkalinity is sufficient. Primary endpoints should include effluent COD, NH_4–N, PO_4–P, and SVI, with pH/alkalinity tracking, as well as weekly metal scans of WAS to confirm regulatory compliance. Statistical analysis will follow the pre-specified LME (Dose × Addition Point), reporting effect sizes with 95% CIs and Holm-adjusted p-values. Scenario TEA should monetize avoided chemicals (alkalinity, micronutrients, polymers), energy effects, and sludge management savings per m^3 and per kg removed, with sensitivity to CM moisture and logistics.

4.8 Environmental and regulatory considerations

CM leachate testing (TCLP/EN 12457) must confirm that metal release remains below biosolids/reuse thresholds at the selected doses. Because CM provides alkalinity as $CaCO_3$ equivalents, its use could reduce off-site transport and storage hazards associated with high-pH reagents. Dust control and secondary containment are essential in handling; at full scale, covered slurry tanks and interlocks on peristaltic pumps mitigate spill risk. If phosphorus capture is observed with Fe dosing, sidestream recovery (struvite) may be evaluated to avoid unintended scaling and to valorize P resources [2].

4.9 Conclusions

CM, when paired with moderate $FeSO_4$ dosing and low-shear hydrodynamics, provides a robust and low-cost pathway to improve settleability while maintaining a neutral pH, which is key for stable nitrification and effluent quality. The convergent chemistry–hydrodynamics window identified here is operationally attainable in municipal ASPs and merits validation in continuous pilots with integrated mass balances, dewaterability metrics, and techno-economic synthesis.

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