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Sequential Cr(VI) Reduction by Sodium Thiosulfate Pentahydrate Followed by CaO-Assisted Alkaline Precipitation in Settling Pond Wastewater

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ABSTRACT

Settling pond wastewater containing hexavalent chromium, Cr(VI), requires sequential treatment that addresses oxidation state and aqueous-phase removal. Five settling ponds were screened, and SP1 and SP2 were selected as high-Cr(VI) matrices. Treatment used 0.45 µm-filtered aliquots. Cr(VI) reduction was evaluated at pH 3.0-3.3 using nominal sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) doses of 1-6 mg/L and contact times of 5, 15, 30, and 60 min, followed by CaO-assisted alkaline precipitation using 0.1-0.6 g CaO per 300 mL at 100, 150, and 200 rpm. Each treatment condition consisted of one process run, while Cr(VI) and total chromium were measured in analytical triplicate; responses were therefore interpreted descriptively. A 1.00 mg/L working solution prepared from a CRM certified for total chromium gave an apparent Cr(VI)-to-certified-total-Cr response ratio of 90.861% (RSD 0.373%, n = 12), which was not interpreted as Cr(VI) recovery because chromium speciation was not certified. At 5 mg/L $Na_2S_2O_3 \cdot 5H_2O$ and 30 min, Cr(VI) decreased to 0.022 mg/L in SP1 and 0.030 mg/L in SP2. Subsequent treatment with 0.6 g CaO per 300 mL produced Cr(VI) <0.004 mg/L and total chromium of 0.050 and 0.030 mg/L. Minimum combined-process Cr(VI) removals were >99.63% and >99.68%, while estimated aqueous total-chromium removals were 95.73% and 97.39%. The process is suitable for laboratory screening, but independent treatment replication, a reagent-free acidic control, unfiltered-matrix validation, species-specific Cr(VI) validation, controlled precipitation-pH experiments, and direct solid-phase characterization remain necessary before confirmatory optimization and scale-up.

1. Introduction

Hexavalent chromium, or Cr(VI), is classified as a priority pollutant because its oxyanion species are highly mobile in aquatic environments, exhibit high toxicity, and can induce oxidative stress, cellular damage, systemic disorders, and carcinogenic effects [1], [2], [3], [4]. The environmental behavior of chromium strongly depends on its oxidation state. Cr(VI) is generally more soluble and bioavailable, whereas trivalent chromium, or Cr(III), has lower mobility and can form sparingly soluble hydroxides under controlled alkaline conditions [1], [3], [4]. Chromium speciation also varies with pH. Hydrogen chromate and dichromate species predominate under acidic conditions, whereas chromate becomes increasingly important at neutral to alkaline pH values [5], [6]. These differences indicate that treatment strategies based solely on total chromium are insufficient because a low total chromium concentration may still contain a hazardous Cr(VI) fraction.

Industrial sources of chromium include metal plating and finishing, mineral processing, leather tanning, pigment production, and other activities that generate chromium-containing liquid residues. Various treatment technologies have been developed, including adsorption, electrocoagulation, membrane separation, photocatalysis, biological reduction, and chemical reduction followed by precipitation [7], [8], [9]. Recent studies have also demonstrated photocatalytic Cr(VI) reduction and

electrochemical treatment routes involving reduction, precipitation, or coagulation mechanisms [10], [11], [12]. Advanced treatment methods can achieve high removal efficiencies, but their application often depends on specialized materials, substantial energy inputs, or complex residue management. In contrast, chemical reduction and hydroxide precipitation use readily available reagents and can be integrated into conventional wastewater treatment systems. However, their effectiveness remains influenced by reaction pH, reducing-agent dosage, contact time, mixing conditions, precipitation pH, solid-liquid separation, and the composition of the actual wastewater matrix. A specific knowledge gap remains because few studies evaluate sequential thiosulfate reduction followed by lime-based precipitation in actual settling-pond wastewater while simultaneously considering analytical detection limits, matrix variability, and the distinction between analytical repeat measurements and independent process replication. This gap motivated the present process-screening design.

Common aqueous Cr(VI) reductants include ferrous salts and sulfur(IV) reagents such as sulfite or bisulfite. Ferrous systems can couple Cr(VI) reduction with formation of Fe(III)-bearing hydroxide solids and co-removal, but they may increase the mass of iron-containing sludge; soluble sulfur-based reductants are readily dosed but remain strongly pH-dependent and add sulfur oxyanions to the treated matrix [7], [8], [13]. Sodium thiosulfate was selected because it is highly soluble, can act as an electron donor, and has field-scale evidence supporting Cr(VI) reduction and immobilization potential when combined with alkaline and binding materials [14]. Its limitations are also relevant: acidic conditions can accelerate thiosulfate decomposition, and the terminal sulfur oxidation products depend on pH, dissolved oxygen, and matrix composition [15], [16]. For the alkaline stage, chromium hydroxide precipitation can be promoted with soluble alkalis such as NaOH or with lime reagents such as $Ca(OH)_2$ and CaO [9], [17]. Quicklime was selected as a lime-based alkalinity source that hydrates to $Ca(OH)_2$ and supplies hydroxide, but CaO addition simultaneously changes reagent dose and pH and can increase calcium-containing solids and sludge. These advantages and limitations were therefore treated as operating trade-offs rather than evidence that $Na_2S_2O_3 \cdot 5H_2O$ and CaO are universally superior to other reagents.

Most previous studies have examined Cr(VI) reduction, chromium precipitation, or solid-waste stabilization as separate treatment processes [18], [19]. However, studies evaluating sequential sodium thiosulfate reduction followed by quicklime-assisted precipitation in actual settling pond wastewater remain limited. The present work was designed as a laboratory process-screening study to distinguish a minimum effective condition from a more conservative high-removal operating condition, rather than to establish a statistically optimized global optimum. Therefore, this study investigated: (i) the response of Cr(VI) to pH, sodium thiosulfate dose, and contact time; (ii) the response of aqueous chromium to quicklime addition, associated pH change, and stirring speed; and (iii) the overall performance and operating trade-offs of the sequential treatment. Five source waters were initially characterized, after which two high-Cr(VI) cases were selected for treatment screening. Analytical quality, detection and quantification limits, reagent use, final chromium concentrations, and implementation constraints were explicitly considered.

2. Research and Methodology

2.1. Wastewater Samples, Instruments, and Reagents

The study was conducted from May to August 2025 at the Chemistry Laboratory, Testing Center Department, PT Tshingjian Technology Research Indonesia, located within the PT Indonesia Morowali Industrial Park. Five settling pond wastewater samples were initially characterized for pH, iron (Fe),

hexavalent chromium [Cr(VI)], total chromium, and total suspended solids (TSS). The screening characteristics of all five samples are reported in Table 2. Settling Pond 1 was designated as SP1 and Settling Pond 3 as SP2 because they had the two highest measured Cr(VI) concentrations. This was a purposive high-load selection intended to challenge the treatment sequence; it does not establish that SP1 and SP2 are statistically representative of the full spatial or temporal variability of settling-pond wastewater. After the initial characterization and TSS measurement, 1,000 mL of each selected sample was filtered through a 0.45 µm membrane using vacuum filtration, homogenized, and divided into 300 mL treatment aliquots. Thus, the five-sample screening characteristics describe the collected source waters, whereas the process experiments evaluated the 0.45 µm-filtered aqueous fraction. Therefore, this study evaluated dissolved-phase chromium treatment performance rather than complete wastewater remediation including particulate-associated chromium. Operationally, pre-filtration produced a clarified fraction for controlled chemical treatment and UV-Vis analysis and reduced particulate interference. However, it also removed suspended particles and potentially particulate-associated chromium. A paired pre-/post-filtration chromium mass balance was not performed, so the contribution of particulate chromium and the effect of suspended solids on reduction, precipitation, and flocculation cannot be quantified from this dataset. The treatment results should therefore not be generalized to whole, unfiltered settling-pond wastewater without additional validation.

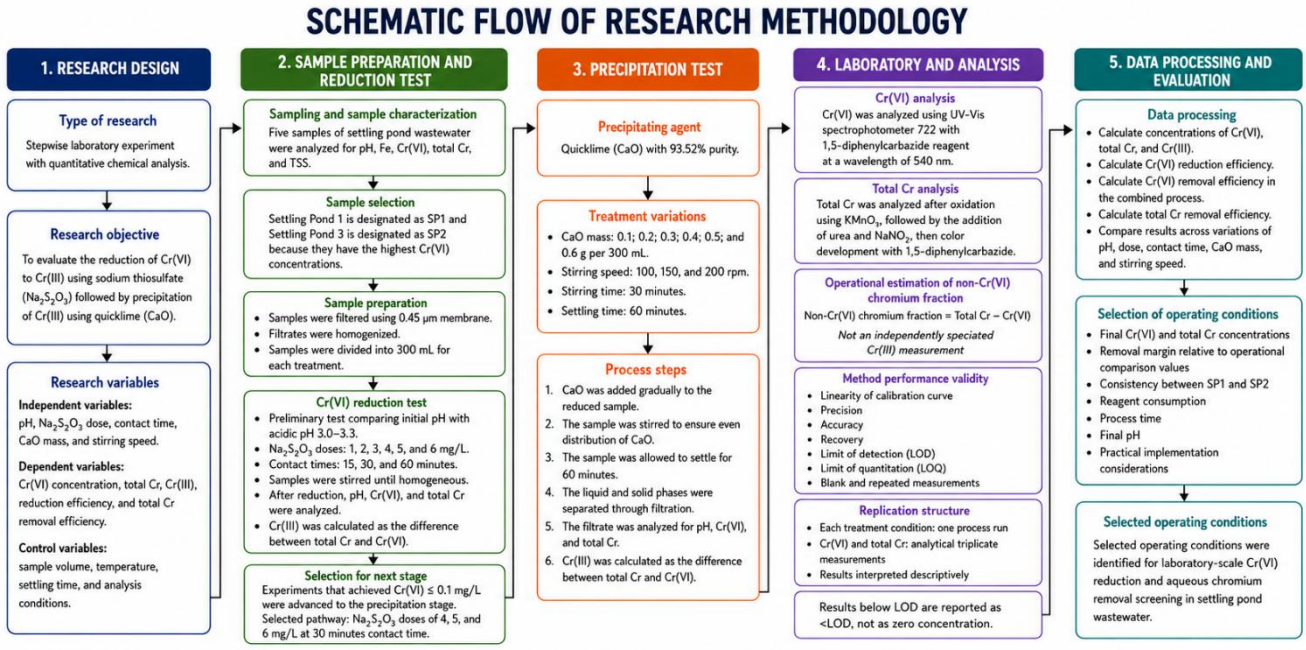

Figure 1. Study design showing process screening, analytical quality assurance, and operating-condition selection.

The primary reagents used in this study included sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$, analytical-reagent grade, purity ≥99.0%, Xilong Scientific), quicklime (CaO) with a purity of 93.52%, potassium dichromate ($K_2Cr_2O_7$), sulfuric acid [H_2SO_4 (1:1)], phosphoric acid [H_3PO_4 (1:1)], 1,5-diphenylcarbazide ($C_{13}H_{14}N_4O$), potassium permanganate ($KMnO_4$), urea, sodium nitrite ($NaNO_2$), and distilled water. The chromium reference stock was a single-element chromium CRM (GSB 04-1723-2004, lot 261004) certified at 1,000 mg/L as total Cr in H_2O. A 1.00 mg/L working solution was prepared by dilution for the repeated analytical check. The certificate assigned total chromium only and did not provide separate certified Cr(VI) and Cr(III) concentrations.

The equipment and instruments used included 20 L sample containers, graduated cylinders, stirring rods, volumetric flasks, graduated pipettes, a hot plate, test tubes, beakers, Pasteur pipettes, Erlenmeyer flasks, a pH meter, a magnetic stirrer, a stopwatch, an analytical balance, a UV-Vis 722 spectrophotometer, a vacuum filtration unit, and an oven.

2.2. Reduction Experiments

Preliminary tests compared samples at their initial pH with samples gradually acidified using H_2SO_4 (1:1) until pH 3.0-3.3 was reached. Each 300 mL filtrate aliquot was treated with $Na_2S_2O_3 \cdot 5H_2O$ at nominal reagent doses of 1, 2, 3, 4, 5, or 6 mg/L, with a contact time of 30 min and a constant stirring speed of 150 rpm. For the 300 mL aliquot volume, these target concentrations correspond to nominal $Na_2S_2O_3 \cdot 5H_2O$ mass equivalents of 0.30, 0.60, 0.90, 1.20, 1.50, and 1.80 mg per treatment, respectively. All dose values reported in mg/L refer to the mass concentration of the pentahydrate reagent as weighed, not to an anhydrous $Na_2S_2O_3$ equivalent. A reagent-free acidic control, consisting of acidified wastewater without $Na_2S_2O_3 \cdot 5H_2O$, was not included in the original experimental design. Consequently, the preliminary comparison evaluates thiosulfate-treated samples under two pH regimes and cannot independently isolate any effect of acidification in the absence of reductant. Because the acidified thiosulfate-treated samples consistently showed lower residual Cr(VI), the main reduction screening experiments were conducted at pH 3.0-3.3.

The main experiments combined six nominal $Na_2S_2O_3 \cdot 5H_2O$ reagent doses with contact times of 5, 15, 30, and 60 min at a constant stirring speed of 150 rpm, resulting in 24 treatment combinations for each sample. The reagent was added gradually while the samples were stirred until homogeneous. After the specified contact time, the samples were analyzed for pH, Cr(VI), and total chromium. Cr(III) was operationally estimated as the difference between total chromium and Cr(VI); it was not independently speciated. The thiosulfate doses were selected empirically rather than from a single fixed stoichiometric requirement because the terminal sulfur oxidation products were not measured. At the selected nominal dose of 5 mg/L, the 99.0% pure $Na_2S_2O_3 \cdot 5H_2O$ corresponds to approximately 1.99×10^{-5} mol $S_2O_3^{2-}$/L, giving molar $S_2O_3^{2-}$:initial-Cr(VI) ratios of approximately 1.02:1 for SP1 and 0.90:1 for SP2. These ratios are process-dose ratios, not unique reaction stoichiometries. For comparison, the idealized tetrathionate pathway, $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$, would require 3 mol $S_2O_3^{2-}$ per mol Cr(VI) reduced to Cr(III), whereas complete oxidation of thiosulfate toward sulfate would correspond to a lower idealized requirement of 0.375 mol $S_2O_3^{2-}$ per mol Cr(VI). Because residual thiosulfate and terminal sulfur species were not determined, the actual sulfur pathway and stoichiometric demand in the wastewater matrix remain unresolved [15], [16]. Actual thiosulfate demand can also exceed an idealized chromium-only electron balance because dissolved oxygen, other oxidizing constituents, and acid-promoted thiosulfate decomposition may consume reductant without directly reducing Cr(VI). These competing demands were not quantified because dissolved oxygen, residual thiosulfate, ORP, and sulfur products were not measured. Therefore, reagent dosage was selected empirically based on observed treatment response rather than calculated stoichiometric demand alone.

2.3. Precipitation Experiments

Reduction treatment pathways that produced Cr(VI) concentrations of ≤0.1 mg/L were subjected to the precipitation stage. Reduction using nominal $Na_2S_2O_3 \cdot 5H_2O$ reagent doses of 4, 5, and 6 mg/L with a contact time of 30 min met this criterion for both samples. The precipitation experiments were conducted sequentially. First, the effect of stirring speed was evaluated using samples reduced with 4

mg/L $Na_2S_2O_3 \cdot 5H_2O$ for 30 min. Nominal quicklime masses of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 g per 300 mL were tested at stirring speeds of 100, 150, and 200 rpm for 30 min. After 150 rpm was selected, quicklime masses ranging from 0.1 to 0.6 g per 300 mL were evaluated for the reduction pathways using 4, 5, and 6 mg/L $Na_2S_2O_3 \cdot 5H_2O$.

The nominal dosage range was equivalent to 0.33-2.00 g/L of quicklime material, or approximately 0.31–1.87 g/L of active CaO based on a purity of 93.52%. Quicklime was added gradually while the samples were stirred to promote uniform dispersion. After 30 min of stirring, the suspensions were covered and allowed to settle for 60 min. The filtrates were then separated using filter paper and analyzed for pH, Cr(VI), and total chromium. The non-Cr(VI) chromium fraction was operationally estimated as total chromium minus Cr(VI); this was not an independently speciated Cr(III) measurement. Because CaO addition simultaneously changed reagent dose and solution pH, the experimental design did not independently control precipitation pH. Consequently, the precipitation data were interpreted as the combined response to CaO addition and its associated alkalization, not as an isolated causal effect of CaO mass at constant pH.

2.4. Chromium Measurement and Quality Assurance

Cr(VI) was analyzed using a 1,5-diphenylcarbazide-based UV-Vis spectrophotometric method at 540 nm with a 2 cm cuvette. In the acidic analytical medium, Cr(VI) oxidizes 1,5-diphenylcarbazide to diphenylcarbazone and is simultaneously reduced to Cr(III); the resulting Cr(III)-diphenylcarbazone complex produces the measured reddish-purple response [20], [21]. Total chromium was analyzed after Cr(III) had been oxidized to Cr(VI) using potassium permanganate, followed by removal of excess oxidant with urea and $NaNO_2$ before color development. For each treated sample, three aliquots from the same process sample were analyzed for Cr(VI) and total chromium. These triplicate measurements were analytical replicates used to assess measurement repeatability and were not independent treatment replicates. Unless otherwise stated, treatment concentrations reported in the tables and figures are the arithmetic means of these three analytical determinations from the same process sample. The analytical triplicates were not used to estimate between-treatment variability or to generate treatment-level inferential statistics. Calibration standards were prepared at 0.00, 0.01, 0.05, 0.10, 0.50, and 1.00 mg/L. Because a Cr(VI)-specific CRM was not available, the 1.00 mg/L working solution prepared from the total-chromium CRM was analyzed with the Cr(VI) procedure only as an analytical response and repeatability check. Its certified total-Cr value was not treated as a species-specific assigned value for Cr(VI). The same 1.00 mg/L working solution was also analyzed using the total-chromium procedure, for which the assigned working concentration derived from the certified total-Cr stock and the analytical measurand were directly comparable. Method performance was therefore evaluated using blanks, calibration linearity, repeatability, the total-Cr CRM recovery, and blank-based estimated detection and quantification limits [22], [23].

LOD and LOQ were estimated from repeated blank responses using LOD = 3s/m and LOQ = 10s/m, where s is the standard deviation of blank absorbance (n = 10) and m is the slope of the corresponding calibration curve. For Cr(VI), s = 0.0004830 and m = 0.3875; for total chromium, s = 0.0005270 and m = 0.4008. These calculations yielded LOD/LOQ values of 0.0037/0.0125 mg/L for Cr(VI) and 0.0039/0.0131 mg/L for total chromium. Because these limits were derived from blank variability and calibration slopes, they are reported as blank-based estimates rather than experimentally verified low-level quantitation limits [22], [23].

Analyte concentrations were calculated from the linear regression equation using the appropriate dilution factor. Cr(III) was operationally estimated by difference as total chromium minus Cr(VI). This

difference is not an independently speciated Cr(III) measurement and combines uncertainty from both analytical determinations. Process efficiency was calculated as $[(C_{initial} - C_{final})/C_{initial}] \times 100\%$. Results below the LOD were reported as <LOD and were not interpreted as zero. Results between the LOD and LOQ were treated as detected but semiquantitative and were not used to claim precise differences between closely spaced treatment conditions. For conservative efficiency calculations when Cr(VI) was <LOD, the LOD was used as the upper-bound final concentration. For context, the WHO drinking-water guideline addresses total chromium at 0.05 mg/L, and was not used to define the wastewater criterion in this study [24]. The values of 0.1 mg/L for Cr(VI) and 0.5 mg/L for total chromium were adopted from the Group I generic wastewater limits in Article 14 and Appendix XLVII of Indonesian Ministry of Environment Regulation No. 5/2014 solely as operational comparison values [25]. They were not used as proof of regulatory compliance, which depends on the applicable sector-specific standard and permit conditions.

2.5. Selection and Interpretation of Operating Conditions

The minimum effective reduction dose was defined as the lowest $Na_2S_2O_3 \cdot 5H_2O$ reagent dose that produced Cr(VI) ≤0.1 mg/L in both samples under the tested conditions. Contact time was selected at the point where extending the reaction produced little additional reduction. The practical precipitation stirring speed was selected from the observed plateau in calculated chromium removal, without claiming measured energy optimization or floc-size optimization. The minimum effective CaO addition was defined as the lowest tested addition that produced Cr(VI) ≤0.1 mg/L and total chromium ≤0.5 mg/L in both samples. A separate selected high-removal condition was identified when a higher reagent dose produced a substantially larger concentration margin across both matrices. These two conditions were treated as different operating trade-offs rather than as a single mathematically unique optimum.

2.6. Replication Structure and Descriptive Analysis

The original experiment was not a fully replicated factorial design. Each treatment combination was represented by one process run, while triplicate aliquots were used only for analytical measurement; the reported concentration for each condition is therefore a mean of analytical determinations from a single process run. Accordingly, analytical triplicate dispersion was not presented as experimental treatment variability, and treatment-level ANOVA, hypothesis tests, and p-values were not calculated because treating analytical triplicates as independent experimental replicates would constitute pseudoreplication. Treatment responses were evaluated descriptively using concentration changes, removal efficiencies, monotonicity, incremental gains, agreement between SP1 and SP2, and consistency between separately generated experimental series. The acidified 30 min condition occurred in both the preliminary pH series and the main dose-time series; these two series were used as a limited internal concordance check but not as a substitute for planned independent replication. No recovery-based correction or bias-sensitivity adjustment was applied to Cr(VI) results because the available CRM was certified for total chromium only and did not provide a species-specific certified Cr(VI) value. To examine the numerical influence of the 90.861% Cr(VI)-to-certified-total-Cr response ratio without misclassifying that ratio as recovery, a non-corrective sensitivity exercise was also performed for the 30 min dose-selection step. Measured Cr(VI) concentrations were divided by 0.90861 only as a hypothetical uniform-response scenario. This exercise was not used to correct the primary dataset because the CRM did not provide a certified Cr(VI) value.

3. Results and Discussion

3.1. Analytical Performance

The Cr(VI) calibration equation was y = 0.3875x − 0.0006 (R^2 = 0.9995), whereas the total chromium equation was y = 0.4008x − 0.0002 (R^2 = 0.9995). Repeated analysis of the 1.00 mg/L working solution prepared from the total-Cr CRM using the Cr(VI) procedure yielded a mean apparent Cr(VI) concentration of 0.9086 mg/L (SD = 0.00339 mg/L; RSD = 0.373%; n = 12). Relative to the certified total-chromium concentration, this corresponds numerically to an apparent Cr(VI)-to-certified-total-Cr response ratio of 90.861%. However, because the CRM certificate did not specify the Cr(VI) and Cr(III) fractions, 90.861% was not interpreted as Cr(VI) recovery and the corresponding -9.139% difference was not interpreted as species-specific analytical bias. The difference may reflect chromium speciation in the CRM, method response, or both, and these contributions cannot be separated using the available data. Thus, this experiment supports good repeatability of the Cr(VI) measurement at this concentration but does not independently establish species-specific Cr(VI) trueness. In contrast, analysis of the same 1.00 mg/L working solution by the total-chromium procedure yielded a mean of 1.0055 mg/L (RSD = 0.628%; n = 10), corresponding to a total-Cr recovery of 100.548% and a relative bias of +0.548%, because the certified and measured quantities were directly comparable.

Table 1. Analytical performance characteristics of chromium determination using UV-Vis spectrophotometry. The Cr(VI) reference comparison is an apparent response ratio to certified total Cr, not a species-specific Cr(VI) recovery.

Parameter	Cr(VI)	Total Cr
Calibration equation	(y = 0.3875x - 0.0006)	(y = 0.4008x - 0.0002)
R^2	0.9995	0.9995
Replicates at 1.00 mg/L	12	10
Mean measured concentration (mg/L)	0.9086	1.0055
RSD (%)	0.373	0.628
Reference comparison at 1.00 mg/L (%)	90.861 apparent Cr(VI)/certified total-Cr response ratio	100.548 total-Cr recovery (+0.548% bias)
LOD (mg/L)	0.0037	0.0039
LOQ (mg/L)	0.0125	0.0131

The blank-based estimated Cr(VI) LOD and LOQ were 0.0037 and 0.0125 mg/L, respectively; the corresponding blank-based total chromium values were 0.0039 and 0.0131 mg/L. The 0.01 mg/L calibration point therefore lies below the theoretical LOQ and was not treated as evidence of validated quantitative performance at 0.01 mg/L. Instrument-derived values below the LOD were reported as <LOD, while values between the LOD and LOQ were interpreted only semiquantitatively. This convention prevents zero-concentration or 100% removal claims beyond the demonstrated analytical capability.

Dose selection was therefore based on the directly measured treatment results rather than on a recovery correction. At 30 min, the 4 mg/L $Na_2S_2O_3 \cdot 5H_2O$ condition produced 0.0841 mg/L Cr(VI) in SP1 and 0.0919 mg/L in SP2, leaving absolute margins of only 0.0159 and 0.0081 mg/L below the 0.1 mg/L operational comparison value. At 5 mg/L, the corresponding concentrations were 0.0222 and 0.0299 mg/L, increasing the margins to 0.0778 and 0.0701 mg/L. Increasing the dose to 6 mg/L lowered the concentrations to 0.0144 and 0.0152 mg/L, but these values approached the Cr(VI) LOQ and the additional decrease was comparatively small. This directly measured concentration margin, together with cross-matrix consistency and the low-end quantification limit, was used to support selection of 5 mg/L as the higher-margin reduction condition. As a sensitivity check only, dividing these measured concentrations by 0.90861 would give 0.0926 and 0.1011 mg/L at 4 mg/L for SP1 and SP2, respectively; 0.0244 and 0.0329 mg/L at 5 mg/L; and 0.0158 and 0.0167 mg/L at 6 mg/L. Under this hypothetical scaling, the 4 mg/L result in SP2 would lie marginally above the 0.1 mg/L operational comparison value, whereas the 5 mg/L condition would remain well below it in both matrices. This does not validate a recovery correction, but it shows that the selected 5 mg/L higher-margin condition is robust to this conservative sensitivity scenario.

3.2. Initial Wastewater Characteristics

Across the five screened settling ponds, pH ranged from 7.75 to 8.40, Fe from 0.062 to 0.200 mg/L, Cr(VI) from 0.026 to 1.155 mg/L, total chromium from 0.053 to 1.180 mg/L, and TSS from 7 to 764 mg/L (Table 2). SP1 and SP2, originating from Settling Ponds 1 and 3, contained Cr(VI) concentrations of 1.018 and 1.155 mg/L, far above the 0.026–0.066 mg/L measured in the other three screened ponds. They were therefore selected as purposive high-Cr(VI) challenge cases rather than as a statistically representative sample of all pond conditions. In the source-water characterization, Cr(VI) accounted for 86.27% of total chromium in SP1 and 99.06% in SP2. SP1 also had substantially higher source-water TSS (764 mg/L) than SP2 (252 mg/L). However, because treatment aliquots were filtered through 0.45 µm membranes before chemical treatment, these TSS values characterize the source waters and do not represent the suspended-solids load present during the reduction and precipitation experiments. Agreement between SP1 and SP2 therefore supports consistency across two different filtered high-Cr(VI) matrices, but it does not demonstrate treatment performance for unfiltered wastewater or the full variability of the five settling ponds.

Table 2. Initial screening characteristics of all five settling pond wastewater samples and basis for treatment-sample selection.

Settling pond	pH	Fe (mg/L)	Cr(VI) (mg/L)	Total Cr (mg/L)	TSS (mg/L)
1 (SP1; selected)	8.05	0.069	1.018	1.180	764
2	7.75	0.200	0.033	0.060	168
3 (SP2; selected)	8.40	0.062	1.155	1.166	252
4	7.90	0.156	0.066	0.092	164
5	8.30	0.081	0.026	0.053	7

For the selected source waters, total Cr − Cr(VI) gave numerical non-Cr(VI) differences of 0.162 mg/L in SP1 and 0.011 mg/L in SP2. These differences are not independently speciated Cr(III)

measurements. In particular, the 0.011 mg/L difference in SP2 is below the blank-based total-chromium LOQ of 0.0131 mg/L and combines uncertainty from two separate measurements; it was therefore not treated as a precise quantitative Cr(III) concentration or used to support precise initial Cr(III) removal claims. The screening values in Table 2 precede the 0.45 µm treatment-preparation filtration, and no paired pre-/post-filtration chromium balance was available.

3.3. Effect of pH, Reductant Dose, and Contact Time

Lower residual Cr(VI) concentrations were observed under the acidified $Na_2S_2O_3 \cdot 5H_2O$ conditions than under the corresponding initial-pH $Na_2S_2O_3 \cdot 5H_2O$ conditions at every tested dose in both samples. At a dose of 4 mg/L, residual Cr(VI) in SP1 decreased from 0.190 mg/L at the initial pH to 0.082 mg/L under acidified conditions, while SP2 decreased from 0.279 to 0.091 mg/L. This pattern is consistent with the pH-dependent speciation and redox behavior of Cr(VI), because proton participation can increase the oxidizing strength of acidic Cr(VI) species and promote electron transfer [5], [6], [26]. However, no reagent-free acidified control was performed. The experiment therefore does not establish that acidification alone caused Cr(VI) loss and cannot separate an isolated acid effect from pH-enhanced thiosulfate-mediated reduction. The pH finding should be interpreted as a comparative response within thiosulfate-treated samples rather than as a reagent-free causal test.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (1)$$

Thiosulfate can release electrons through several oxidation pathways. One idealized pathway produces tetrathionate, although the actual products may also include sulfate, elemental sulfur, and intermediate sulfur species, depending on pH, dissolved oxygen, and wastewater composition [15], [16]:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \quad (2)$$

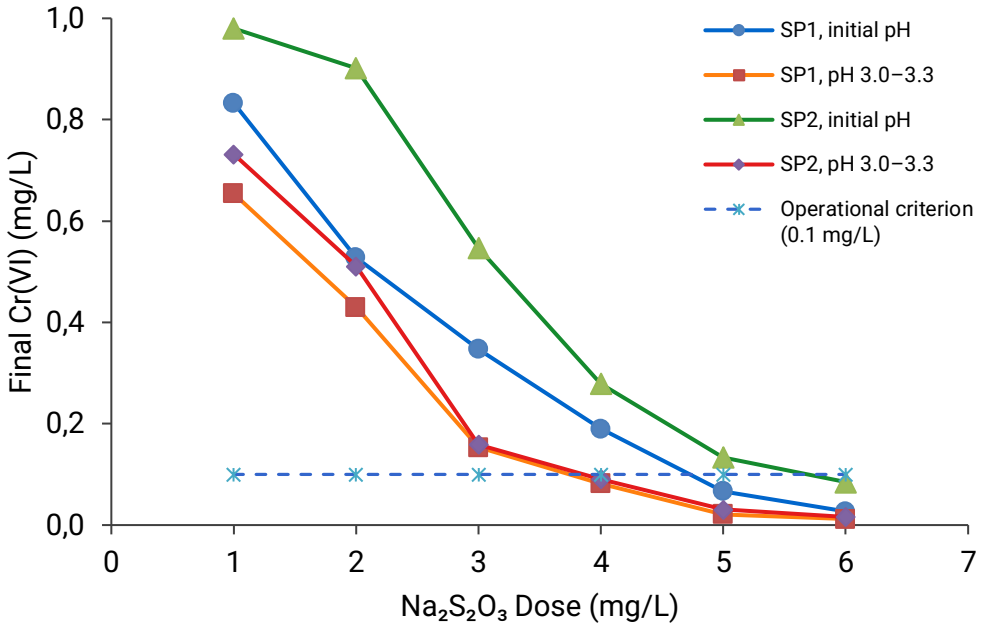

Figure 2. Effects of pH and nominal $Na_2S_2O_3 \cdot 5H_2O$ reagent dose on the final Cr(VI) concentration during the 30 min preliminary test.

In the main dose-time series at 30 min, residual Cr(VI) decreased monotonically with increasing $Na_2S_2O_3 \cdot 5H_2O$ reagent dose. The 4 mg/L condition produced 0.0841 mg/L in SP1 and 0.0919 mg/L in SP2 and was therefore the minimum nominally effective dose. However, these values were only 0.0159

and 0.0081 mg/L below the 0.1 mg/L operational comparison value. At 5 mg/L, concentrations decreased to 0.0222 and 0.0299 mg/L, providing substantially larger margins of 0.0778 and 0.0701 mg/L. At 6 mg/L, concentrations decreased further to 0.0144 and 0.0152 mg/L, only slightly above the Cr(VI) LOQ. A useful internal concordance check was available because the acidified 30 min condition was also tested in the preliminary pH series. Across the six doses, the mean absolute difference between the preliminary and main 30 min series was 0.0017 mg/L for SP1 and 0.0006 mg/L for SP2, and the maximum absolute difference was ≤0.0030 mg/L. This agreement does not replace independent replication, but it supports the consistency of the observed dose-response pattern under the same nominal conditions. Taken together, the directly measured margins, cross-matrix agreement, and low-end quantification constraint support classifying 4 mg/L as the minimum nominally effective dose and 5 mg/L as the selected higher-margin reduction dose. The observed dose-dependent decrease in Cr(VI) is consistent with previous studies reporting that increasing reductant availability promotes Cr(VI) reduction, although the required reagent dose varies with reductant chemistry, initial chromium concentration, pH, and wastewater matrix [13], [26]. The 6 mg/L condition was not selected because its incremental numerical improvement approached the method's low-end quantification capability and required additional reductant. The dose-response also needs to be interpreted against the electron balance. At the selected nominal 5 mg/L dose, the process supplied approximately 1.99×10^{-5} mol $S_2O_3^{2-}$/L, corresponding to $S_2O_3^{2-}$:initial-Cr(VI) molar ratios of about 1.02:1 in SP1 and 0.90:1 in SP2. These ratios fall between idealized limits associated with different sulfur oxidation endpoints: a tetrathionate pathway would require 3 mol $S_2O_3^{2-}$ per mol Cr(VI), whereas complete oxidation toward sulfate would correspond to a lower idealized requirement of 0.375 mol/mol. Because the terminal sulfur products were not measured, the observed plateau from 5 to 6 mg/L cannot be assigned to a single stoichiometric pathway. Dissolved oxygen, other oxidizing matrix constituents, and acid-promoted thiosulfate decomposition may also consume reductant. These competing reactions provide a plausible explanation for why empirical process dose cannot be inferred from a single theoretical Cr(VI)-only ratio, but they were not quantified in this study.

Table 3. Reduction results after 30 min at pH 3.0–3.3 and a stirring speed of 150 rpm. Dose refers to the nominal $Na_2S_2O_3 \cdot 5H_2O$ reagent concentration as weighed. Reported concentrations are means of three analytical determinations from the same treatment sample; these analytical triplicates are not independent process replicates.

Dose (mg/L)	SP1 Cr(VI) (mg/L)	SP1 Reduction Efficiency (%)	SP2 Cr(VI) (mg/L)	SP2 Reduction Efficiency (%)
1	0.657	35.46	0.732	36.64
2	0.432	57.52	0.512	55.63
3	0.154	84.89	0.159	86.24
4	0.084	91.74	0.092	92.05
5	0.022	97.82	0.030	97.41
6	0.014	98.58	0.015	98.68

Contact time had its largest practical effect between 5 and 30 min. At 5 mg/L $Na_2S_2O_3 \cdot 5H_2O$, Cr(VI) reduction increased from 69.43% to 97.82% in SP1 and from 70.60% to 97.41% in SP2. Extending the treatment to 60 min did not further reduce the measured Cr(VI) concentration at this dose in either sample. This plateau is consistent with a near-stable response over the tested interval, although the experiment did not measure ORP, residual thiosulfate, or kinetic rate constants and therefore cannot

identify the controlling mechanism. A 30 min contact time was selected as the practical screening condition because doubling the contact time did not improve the measured 5 mg/L result.

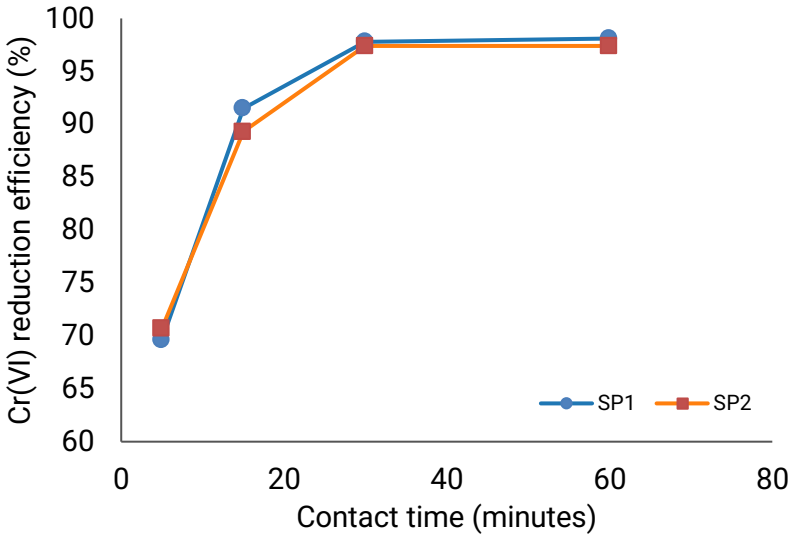

Figure 3. Effect of contact time on Cr(VI) reduction efficiency using a nominal 5 mg/L $Na_2S_2O_3 \cdot 5H_2O$ reagent dose at pH 3.0-3.3 and a stirring speed of 150 rpm.

3.4. Aqueous Chromium Response to CaO Addition and Associated pH Change

The reduction stage markedly decreased the Cr(VI) fraction while leaving dissolved total chromium nearly conserved. At the selected 5 mg/L, 30 min reduction condition, total chromium was 1.178 mg/L in SP1 compared with an initial 1.180 mg/L and 1.161 mg/L in SP2 compared with an initial 1.166 mg/L. These values correspond to approximately 99.84% and 99.54% retention of initial dissolved total chromium, respectively. The near-conservation of total chromium, together with the strong decline in Cr(VI), is consistent with a shift from the measured Cr(VI) fraction toward a non-Cr(VI) dissolved chromium fraction rather than substantial phase removal during reduction. Because Cr(III) was calculated by difference and was not independently speciated, this observation should not be interpreted as direct proof of complete Cr(VI)-to-Cr(III) conversion. Quicklime was subsequently added to raise alkalinity and promote removal of dissolved chromium through hydroxide formation and solid–liquid separation. Idealized reactions are shown below:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (3)$$

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3(s) \quad (4)$$

The stirring-speed series was interpreted descriptively. Because Cr(III) was not independently speciated, the original difference-based metric is described here as removal of the calculated non-Cr(VI) chromium fraction rather than direct Cr(III) removal. Across the six CaO additions, increasing the speed from 100 to 150 rpm increased this difference-based removal metric by an average of 3.63 percentage points in SP1 and 3.23 points in SP2, whereas increasing from 150 to 200 rpm added only 0.58 and 0.55 points, respectively. At 0.6 g CaO, the increase from 150 to 200 rpm was only 0.5 points in SP1 and 0.8 points in SP2. Therefore, 150 rpm was retained as the practical mixing condition for the subsequent CaO series. Energy consumption, particle size, and floc breakage were not measured, so 150 rpm should not be interpreted as an energy-optimized or hydrodynamically proven optimum.

At 150 rpm, dissolved total chromium decreased with increasing CaO addition across the evaluated series. Along the selected 5 mg/L $Na_2S_2O_3 \cdot 5H_2O$ pathway, total chromium in SP1 changed from 0.804 mg/L at 0.1 g CaO to 0.050 mg/L at 0.6 g, while SP2 changed from 0.821 to 0.030 mg/L. The recorded final pH for this same pathway was 9.56, 10.25, 10.15, 10.23, 10.95, and 11.12 at 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 g CaO, respectively. Because CaO addition and precipitation pH changed concurrently, the observed decrease in dissolved chromium cannot be attributed independently to CaO mass or to pH. The results therefore describe their combined operational effect. A 0.4 g CaO addition was sufficient for the minimum effective combined condition, whereas 0.6 g produced the lowest dissolved chromium concentrations along the selected 5 mg/L reduction pathway. The decrease in aqueous chromium with increasing alkalinity is consistent with previous studies showing that alkaline precipitation can effectively remove reduced chromium species from solution, although the effective pH and reagent requirement depend strongly on wastewater composition and initial chromium concentration [9], [17].

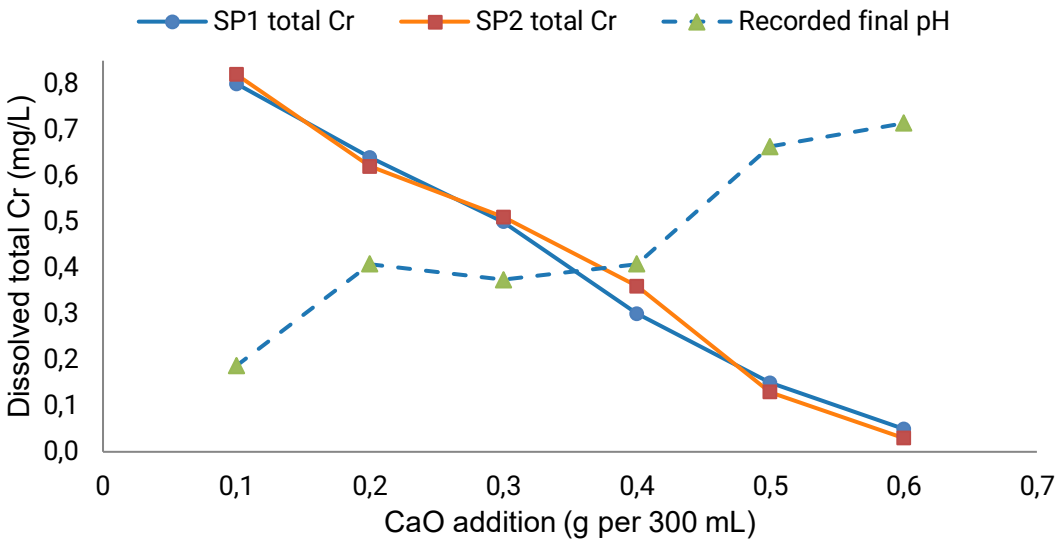

Figure 4. Observed dissolved total chromium concentrations and recorded final pH across increasing CaO additions along the nominal 5 mg/L $Na_2S_2O_3 \cdot 5H_2O$ reduction pathway (30 min reduction, 150 rpm precipitation mixing). The pH series is displayed together with CaO dose to show that reagent addition and alkalization changed concurrently.

CaO addition raised the treated-water pH from approximately 3.09-3.22 before precipitation to 9.50-11.25 after precipitation. At 0.6 g per 300 mL, final pH was approximately 11.10-11.25, including 11.12 along the selected 5 mg/L pathway. These values show that chromium removal and alkalization are operationally coupled in the present dataset. Although the low aqueous chromium concentrations are consistent with hydroxide precipitation and solid separation, the treated effluent cannot be considered ready for discharge or reuse without controlled neutralization and subsequent remeasurement of pH, Cr(VI), and total chromium. The high CaO condition also implies greater reagent consumption and potentially greater sludge generation; sludge mass and composition were not quantified in this study.

3.5. Overall Performance and Selected Operating Conditions

Using 5 mg/L $Na_2S_2O_3 \cdot 5H_2O$ for 30 min at 150 rpm reduced Cr(VI) from 1.018 to 0.022 mg/L in SP1 and from 1.155 to 0.030 mg/L in SP2, corresponding to reductions of 97.82% and 97.41%. After addition of 0.6 g CaO per 300 mL, 30 min mixing at 150 rpm, 60 min settling, and filtration, Cr(VI) was <0.004 mg/L in both samples. Using the LOD as a conservative upper-bound concentration, combined-process

Cr(VI) removal was >99.63% in SP1 and >99.68% in SP2. Final total chromium was 0.050 mg/L in SP1 and 0.030 mg/L in SP2, corresponding to estimated aqueous total-chromium removals of 95.73% and 97.39%. These values quantify aqueous-phase treatment performance only; they do not establish the chemical form or leaching stability of chromium in the separated solids. High Cr(VI) removal has also been reported using photocatalytic and electrochemical treatment systems [10], [11], [12]. However, direct numerical comparison with the present sequential chemical treatment should be made cautiously because those studies employed different reaction mechanisms, reactor configurations, influent characteristics, and treatment endpoints. The present results therefore demonstrate competitive aqueous-phase removal under the tested laboratory conditions, but they do not establish superiority over alternative Cr(VI) treatment technologies.

Table 4. Comparison between the minimum effective condition and the selected high-removal condition.

Criterion	Minimum Effective Condition	Selected High-Removal Condition
$Na_2S_2O_3 \cdot 5H_2O$ reagent dose	4 mg/L	5 mg/L
Reduction contact time	30 min	30 min
Reduction stirring speed	150 rpm	150 rpm
CaO dose	0.4 g/300 mL	0.6 g/300 mL
Precipitation stirring speed	150 rpm	150 rpm
Final Cr(VI) concentration in SP1	0.049 mg/L	<0.004 mg/L
Final Cr(VI) concentration in SP2	0.054 mg/L	<0.004 mg/L
Final total Cr concentration in SP1	0.367 mg/L	0.050 mg/L
Final total Cr concentration in SP2	0.319 mg/L	0.030 mg/L
Total Cr removal in SP1 and SP2	68.88%; 72.57%	95.73%; 97.39%
Main advantage	Lower reagent consumption	Higher removal margin and consistency
Main limitation	Smaller safety margin for Cr(VI)	Higher CaO consumption and final pH

The two conditions in Table 4 represent different operating trade-offs rather than a unique mathematical optimum. The minimum effective condition (4 mg/L $Na_2S_2O_3 \cdot 5H_2O$ and 0.4 g CaO per 300 mL) minimizes reagent use while meeting the operational comparison values in both samples, but it provides a smaller analytical margin for Cr(VI). The selected high-removal condition (5 mg/L $Na_2S_2O_3 \cdot 5H_2O$ and 0.6 g CaO per 300 mL) gives substantially lower final chromium concentrations and greater cross-matrix margin, but at the cost of higher CaO consumption and a final pH around 11. No weighted objective function, response-surface model, or replicated optimization design was used; therefore the higher-removal condition is not claimed to be a global or statistically proven optimum.

The 6 mg/L reduction pathway was not selected because the additional Cr(VI) decrease was close to the analytical LOQ and did not consistently improve final total chromium across both matrices.

3.6. Mechanistic Interpretation and Implementation Constraints

The aqueous-phase results support different operational roles for the two stages but do not directly resolve all chemical mechanisms. During reduction, near-conservation of dissolved total chromium together with a large decline in Cr(VI) is consistent with redox conversion within the dissolved chromium pool. During the CaO stage, the substantial decline in dissolved total chromium after settling and filtration is consistent with transfer of chromium from the filtrate into removed solids. However, the solid phase was not analyzed for Cr(VI), total chromium, mineralogy, or leaching behavior. Accordingly, direct solid-phase chromium characterization was not performed, and this limitation cannot be resolved retrospectively from the aqueous-phase data. The study therefore does not demonstrate that the separated solid was pure $Cr(OH)_3$, identify the chromium-bearing phase, or establish permanent chromium immobilization. The further decline in measured Cr(VI) after CaO addition may reflect continued reduction by residual reductant, adsorption or coprecipitation with newly formed solids, physical entrapment, filtration of chromium-bearing particles, or a combination of these processes. Residual thiosulfate, sulfate, ORP, and sulfur oxidation products were not measured, so these explanations remain mechanistic interpretations rather than experimentally identified pathways.

For confirmatory optimization and scale-up, the most important additions are independent treatment replication, controlled experiments in which precipitation pH and CaO dose are varied separately, and direct characterization of the separated solids. Continuous or pilot systems should monitor pH and ORP and relate reductant dose to the incoming Cr(VI) load. Following precipitation, controlled neutralization should be accompanied by repeat measurements of pH, Cr(VI), and total chromium to evaluate possible redissolution. The sludge should be characterized for total chromium, Cr(VI), moisture content, mineralogical or elemental composition, and leaching potential. These measurements are required before concluding that the process provides stable chromium immobilization rather than aqueous-to-solid transfer alone.

4. Conclusion

This laboratory process-screening study showed a consistent decrease in Cr(VI) with increasing $Na_2S_2O_3 \cdot 5H_2O$ reagent dose and contact time and a consistent decrease in aqueous total chromium with increasing CaO addition in two selected high-Cr(VI) settling-pond matrices. Five settling ponds were initially screened, but SP1 and SP2 were purposively selected because they contained the highest Cr(VI); the two treated cases therefore should not be interpreted as statistically representative of all settling-pond variability. In addition, treatment experiments used 0.45 µm-filtered aliquots, so performance applies to the filtered aqueous fraction rather than whole unfiltered wastewater. The experimental design used one process run per treatment condition with analytical triplicate measurements, so the findings support descriptive process selection rather than inferential statistical optimization. A 4 mg/L $Na_2S_2O_3 \cdot 5H_2O$ dose was the minimum nominally effective reduction condition at 30 min, whereas 5 mg/L for 30 min was retained as the selected higher-margin reduction condition, producing 0.022 mg/L Cr(VI) in SP1 and 0.030 mg/L in SP2. The 1.00 mg/L analytical check was a working solution prepared from a CRM certified for total chromium rather than Cr(VI); consequently, its 90.861% apparent Cr(VI)-to-certified-total-Cr response ratio was not interpreted as Cr(VI) recovery or used to correct treatment concentrations. A non-corrective sensitivity analysis nevertheless showed that the 5 mg/L condition remained below the 0.1 mg/L comparison value in both matrices under

hypothetical scaling by 0.90861. Subsequent addition of 0.6 g CaO per 300 mL produced Cr(VI) <0.004 mg/L and total chromium of 0.050 mg/L in SP1 and 0.030 mg/L in SP2, corresponding to minimum combined-process Cr(VI) removals >99.63% and >99.68% and estimated aqueous total-chromium removals of 95.73% and 97.39%. CaO addition simultaneously increased final pH to approximately 11, so CaO-dose and precipitation-pH effects could not be separated and the high-removal condition is not a statistically proven global optimum. No reagent-free acidic control was included, so the observed advantage of acidified thiosulfate treatment cannot be attributed to acidification alone. The study demonstrates aqueous-phase treatment performance but does not directly identify the chromium-bearing solid or establish its long-term stability. Confirmatory work should prioritize independent treatment replication, paired unfiltered-versus-filtered wastewater tests, an acid-only control, a Cr(VI)-specific reference or matrix-spike validation across the low concentration range, controlled CaO-versus-pH experiments, measurements of residual sulfur species and ORP, and direct solid-phase chromium and leaching characterization.

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- **AI Use Declaration:** The authors used ChatGPT (OpenAI) to assist with grammar and spelling checks, language editing, translation, text organization, and limited technical assistance. All AI-generated outputs were reviewed and verified by the authors. The authors remain fully responsible for the accuracy, originality, integrity, and scientific content of the manuscript.
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