

OXIDATIVE REGENERATION OF IRON FOR TREATMENT PLANT PURPOSES

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ABSTRACT

The Orange County Sanitation Districts (OCS D) currently utilize PRI-SC™ technology to control hydrogen sulfide emissions within its collection system. With PRI-SC™, ferrous chloride (FeCl₂) is added for sulfide control and then the combined iron is regenerated using hydrogen peroxide (H₂O₂). OCS D also adds ferric chloride (FeCl₃) at its treatment plants to enhance solids separation (CEPT). We previously reported on the improved sulfide control efficiencies in the collection system using PRI-SC™; however, little data were available at the time on regenerating that iron a second time (at the treatment plant) to benefit CEPT. This paper discusses the economic and performance benefits of doing so using hydrogen peroxide and bleach at OCS D Plant No. 2. The study involved beaker tests, jar tests and field trials, as well as an analysis of the historical plant records.

The results show that maximizing the overall cost performance of all relevant chemical additions at the plant (H₂O₂, FeCl₃, bleach, polymer) requires that the influent sulfide be removed and the ferrous portion of the influent iron (from PRI-SC™) be oxidized to ferric iron. Significantly, this oxidized ferric iron was shown to have flocculation performance similar to that of FeCl₃. It was further shown that (generally) H₂O₂ is the more cost-effective oxidant for both sulfide and ferrous iron oxidations. However, since the plant already adds an excess of bleach to the primaries for disinfection, we found it to be practically more efficient to allow the bleach to oxidize the ferrous iron. Thus, the recommendation of this work was to remove residual levels of sulfide from the influent sewers using H₂O₂; and to allow the ferrous iron to be oxidized later by the bleach disinfectant. Conversion of ferrous iron to ferric iron was essentially 100%, resulting in a contribution to Plant No. 2 of ca. 7,000 lbs-Fe³⁺ per day. The cost for additional bleach to oxidize this Fe²⁺ was ca. \$2000, yielding an effective cost of ca. \$0.30 per lb-Fe³⁺. This represents a 40% savings over adding additional FeCl₃.

KEYWORDS

Hydrogen sulfide, chemically enhanced primary treatment, iron salts, hydrogen peroxide, sodium hypochlorite

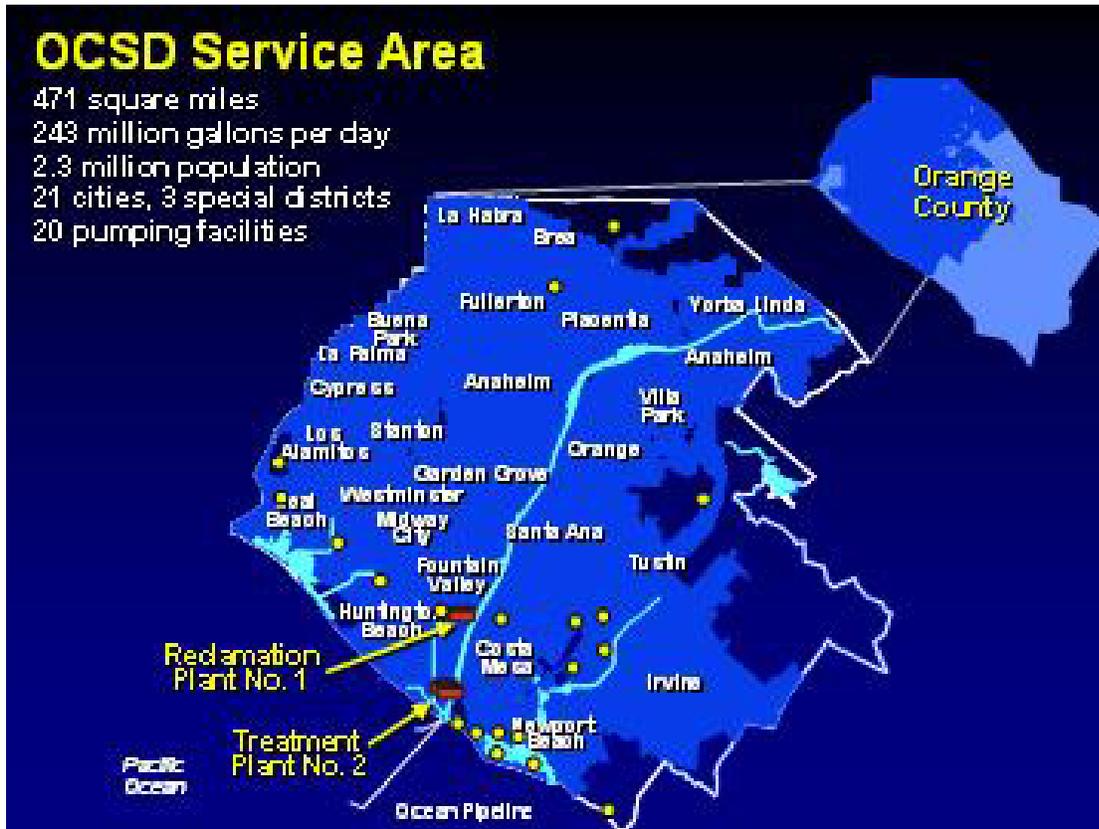
INTRODUCTION

Orange County Sanitation District

The Orange County Sanitation District (OCS D) operates two treatment plants that process a combined flow of 240 mgd. Plant No.1 provides 65 mgd primary and secondary treatment, and

Plant No.2 (the focus of this study) provides 100 mgd primary treatment and 75 mgd primary and oxygen activated sludge secondary treatment. The combined effluent from both plants (60% secondary and 40% primary) is discharged to the Pacific Ocean 4.5 miles offshore.

Figure 1. Orange County Sanitation Districts, California: Service Area



In the 1970's, OCSD was granted a 301(h) waiver from the full secondary treatment requirements of the Federal Clean Water Act. Consistent with the 1983 California Ocean Plan and local basin requirements, the NPDES permit allowed a discharge blend of secondary and primary effluent, but the BOD and TSS permit limits were based on a fixed mass discharge. Hence, as the OCSD service population grew, additional treatment in the form of secondary treatment or chemically-enhanced primary treatment (CEPT) was needed. Studies into CEPT were initiated in the 1970's by several of the Southern California utilities, and full-scale CEPT was implemented at both OCSD plants in the 1980's.

CEPT involves adding of ferric chloride (FeCl_3) and anionic polymer to the primary influent to obtain a clear effluent substantially free from colloidal and suspended matter (Hassan, 1990; Harleman, 1992; Foess, 2003). While the degree of clarification obtained depends on the quantity of chemicals used and the care with which the process is controlled, TSS removals at OCSD were typically improved from 40-60% to 80-90%, and BOD removals were improved from 30-40% to 40-70% (Ooten, 1986). This level of performance was achieved by adding 6-8 mg/L Fe^{2+} and 0.2–0.3 mg/L polymer. However, two significant events impacted CEPT operations at Plant No.2 in August 2002:

- 1) OCSD implemented a novel technology for collection system sulfide control that uses ferrous chloride (FeCl_2) and H_2O_2 , termed PRI-SCTM (Peroxide Regenerated Iron – Sulfide Control); and
- 2) OCSD began adding sodium hypochlorite into the influent of the primary clarifiers to provide disinfection of the primary effluent (contact times were insufficient for disinfecting after the clarifiers).

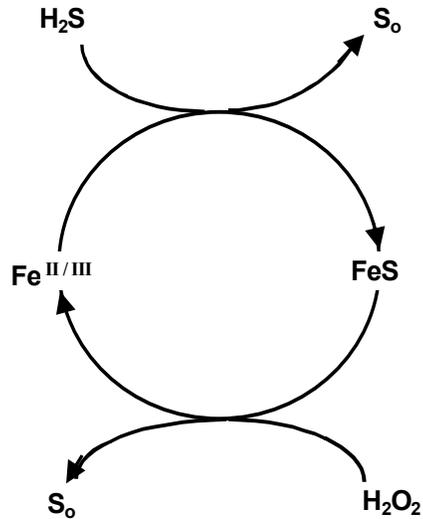
We previously reported on the sulfide control efficiencies in the collection system using PRI-SCTM (Walton, 2003). Treatment plant aspects of that study (to assess the utility of iron contributed by PRI-SCTM for CEPT) were limited to the final 30 days. Though abbreviated, the results indicated a positive impact evidenced by increasing doses of H_2O_2 into the PRI-SCTM influent sewers being accompanied by lower TSS levels in the clarifier effluent. Alternatively, similar TSS levels were obtained at reduced FeCl_3 feed rates. This paper expands on the CEPT aspects of using hydrogen peroxide and/or bleach to oxidize sulfide and ferrous iron present in the wastewater, and discusses the economic and performance benefits of doing so.

The PRI-SCTM and PRI-CEPTTM technology

The Peroxide Regenerated Iron technology, whether for Sulfide Control (PRI-SCTM) or for Chemically-Enhanced Primary Treatment (PRI-CEPTTM) involves using iron salts as the primary agent, and adding H_2O_2 to regenerate and/or oxidize the iron (as Fe^{2+} and FeS) at one or more points downstream. In the case of PRI-SCTM, the analogy is one of a capturing agent (iron salt) added at the top of an interceptor, which then adsorbs dissolved sulfide as it moves down the line. Intermittent H_2O_2 injection serves to regenerate the capturing agent thereby allowing additional sulfide to be absorbed downstream. At the final regeneration point (the treatment plant), H_2O_2 is added to produce a hydrous ferric oxide oxidation product that is available to enhance primary clarification (PRI-CEPTTM). The combination treatment may thus be viewed as a regeneration cycle, with an oxidant (H_2O_2) oxidizing the inactive iron (FeS or Fe^{2+}) *in-situ* – yielding ferrous / ferric iron and colloidal sulfur. By pushing the reaction with excess H_2O_2 , ferric iron is favored.

Figure 2. Peroxide Regenerated Iron – Sulfide Control (PRI-SC)TM

Representation of the regeneration cycle



Inputs: Ferrous iron
Hydrogen sulfide
Hydrogen peroxide

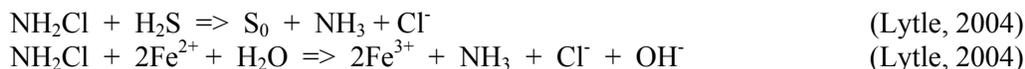
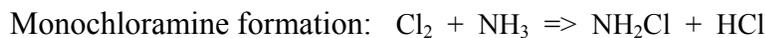
Outputs: Elemental sulfur
Ferric iron

This paper will show that (in addition to H_2O_2 , and if warranted in such situations as OCSD Plant No. 2), the oxidizing agent used to drive the cycle can be sodium hypochlorite bleach (or more accurately, the monochloramine formed upon its addition to wastewater). The reaction equations involved in the regeneration cycle have been reported as:

For hydrogen peroxide:



For bleach (sodium hypochlorite):



Economic Driver

While the amount of ferric iron needed for CEPT is typically 6-8 mg/L, any amount of Fe added to the collection system can potentially contribute to CEPT provided that it is first converted to ferric iron. In the case of OCSD Plant No. 2, PRI-SC™ treatment within the collection system contributed ca. 7,500 lbs-Fe per day (or ca. 4.5 mg/L). The amount of oxidant theoretically needed to affect the regeneration depends on the form in which the iron enters the treatment plant. Generally, the influent Fe contributed by PRI-SC™ is comprised of three forms: unassociated ferrous iron (Fe^{2+}), ferrous iron bound as FeS, and ferric iron (Fe^{3+} formed by H_2O_2 added at the trunkline midpoints and/or by natural aeration within the sewer). The ratios of these components change hourly, seasonally and between interceptors; and at OCSD Plant No. 2, their annualized averages in the mixed influent are ca. 20-50-30. Using typical market prices thus puts the theoretical Fe regeneration costs at OCSD Plant No. 2 (as \$ per lb- Fe^{3+}) at \$0.14 for H_2O_2 and \$0.26 for bleach (cf. \$0.47 for additional $FeCl_3$).

Figure 3. The economic case for considering iron recycling

Iron species	Portion of Influent Fe as... mg/L Fe % of Total		Regenerated by H2O2		Regenerated by NaOC	
			Demand wt : wt	Cost \$/lb-Fe3+	Demand wt : wt	Cost \$/lb-Fe3+
Ferrous (Fe2+)	2.3	50%	0.30	\$0.06	0.66	\$0.11
Ferrous sulfide (FeS)	0.9	20%	0.94	\$0.08	2.16	\$0.15
Ferric (Fe3+)	1.4	30%	0.00	\$0.00	0.00	\$0.00
Total costs, \$ per lb-Fe3+				\$0.14	\$0.26	
Purchased FeCl3, \$ per lb-Fe3+				\$0.47	\$0.47	
% savings				71%	44%	
Assumed chemical prices:		FeCl3 price	\$325	per ton-100%		
		H2O2 price	\$0.200	per lb-50%		
		NaOCl price	\$0.450	per gal-12.5%		

Study objectives

The primary objective of this study was to determine the optimal dosages of H₂O₂ and bleach needed to regenerate the 4-5 mg/L of ferrous iron available from using PRI-SC™ in the collection system. It was understood that regardless of the oxidant chosen, bleach would continue to be added to the primary clarifier influent (for disinfection purposes). Thus, to achieve this goal we had to: 1) understand the interactions of six different chemical additions (FeCl₂ and H₂O₂ within the collection system, and H₂O₂, FeCl₃, NaOCl, and anionic polymer at the treatment plant); and 2) balance the doses of H₂O₂ and bleach within actual plant operations to maximize cost-performance in terms of both sulfide control and CEPT. Within this context, the study consisted of lab tests (to characterize chemical interactions and dose-response relationships) and field tests (to track chemical species and assess the practical aspects of ferrous oxidation).

METHODOLOGY

Beaker tests

The beaker tests involved batch treating one liter of ferrous / sulfide solution in either deionized water or wastewater using either H₂O₂ or NaOCl. All samples were purged with N₂ to remove dissolved oxygen prior to sample make-up (which otherwise oxidizes total sulfide). Treated samples were reacted at room temperature and agitated only enough to mix in the reagents. Using these techniques, sulfide losses in the controls were kept to 10-20%. Analytical methods are described in Figure 4 (below). The variables considered were initial ferrous / sulfide levels (2 – 100 mg/L), reaction pH (6, 7 and 8), reaction time (5 – 30 minutes) and oxidant dose (0.5 – 6 times theoretical).

Figure 4. Analytical methods

Analysis	Procedure
Total sulfide	Std. Methods 4500-S2- D. Methylene Blue (Lamotte drop count kit)
Dissolved sulfide	Ditto, using pre-flocculation to remove insoluble sulfides
Total iron	Std. Methods 3500-F D. Phenanthroline (Hach colorimeter)
Ferrous iron	Same as above, without reductive pretreatment
Ferric iron	Calculated by difference (total iron - ferrous iron)
Residual H ₂ O ₂	Enzymatic redox test strips (e.g., EM Quant)
Total chlorine	Std. Methods 3500-F D. (Hach colorimeter)
Total suspended solids	Std. Methods 2450-D
Settleable solids	Std. Methods 2450-F (volumetric)
Turbidity	Hach 890 colorimeter (direct read, FAU)

Jar tests

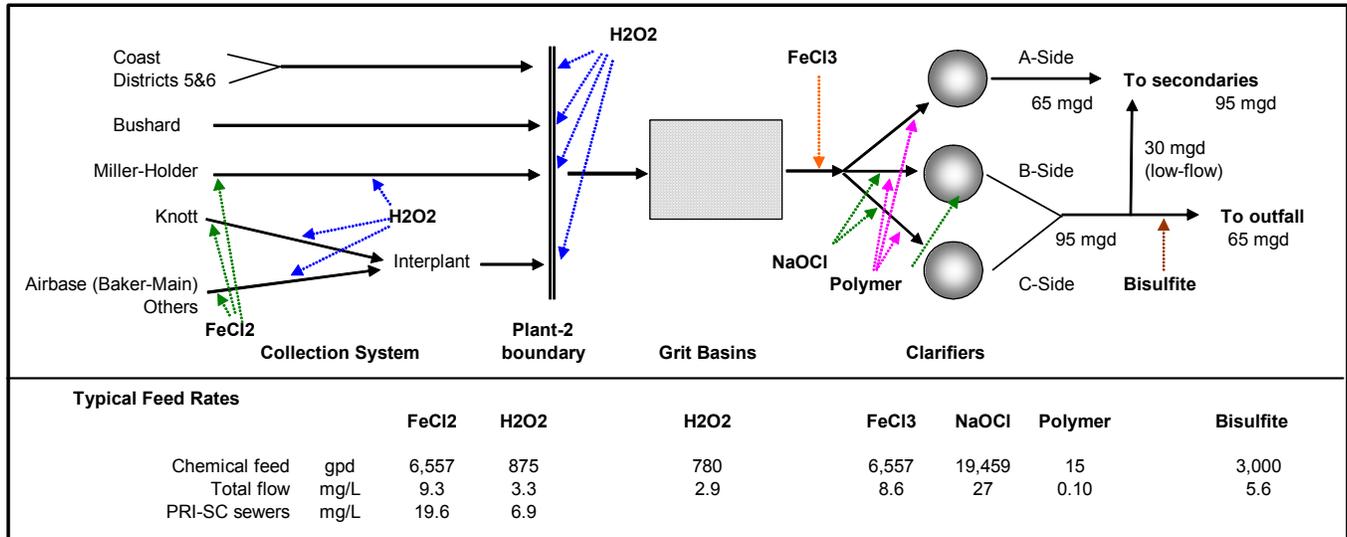
A six-unit jar tester was used to assess CEPT performance and to mimic the chemical additions, wastewater turbulence and reaction times of the treatment plant. Having identified the stir rates that reproduced TSS values in the treatment plant (at similar chemical doses), this set of dosing parameters was designated the ‘control’, and repeated in Jar No.1 for each series of ca. 30 runs (representing ca. 180 different conditions). The conditions varied by the influent levels of ferrous iron and sulfide, and the doses of H₂O₂, FeCl₃, polymer and bleach. Except where noted, no attempt was made to dose the bleach to a 0.5-1.0 mg/L residual (as occurs in the plant). Instead, the bleach dose was set at 26 mg/L (i.e., the average plant dose) regardless of the actual demand within the wastewater sample being tested.

Field tests

Field testing involved sampling plant processes over several days throughout the year to track the relevant chemical species as the wastewater moved from the influent sewer through the primary clarifiers. Two sets of conditions were evaluated: 1) adding H₂O₂ to oxidize the ferrous iron at the influent sewer; and 2) allowing the influent ferrous iron to pass through the headworks to be oxidized by bleach at the clarifier influents.

The flow diagram and sampling program for this work is shown in Figure 5 (below). The flow from the Miller-Holder interceptor received closer scrutiny since it contributes a large portion of the ferrous iron and at significant levels (8-12 mg/L in 23 mgd). The transit time from H₂O₂ injection to the headworks area is ca. 5 minutes whereupon it blends into 140 mgd (containing < 0.2 mg/L sulfide and 4 mg/L Fe – 30-50% of which is ferric). FeCl₃ and NaOCl are added at the end of the grit chambers and diluted polymer is added at the distribution structure for the primary clarifiers. Since bleach is added only to those clarifiers that do not undergo secondary treatment, side-by-side comparisons of bleach / no-bleach scenarios were possible.

Figure 5. Treatment plant flow diagram (showing chemical injections)



RESULTS

Beaker tests

Beaker tests were done to document the reactions of sulfide and ferrous iron with the two oxidants (H₂O₂ and bleach). The results showed that a H₂O₂ dose of 1.0 – 1.5 times stoichiometry into wastewater containing FeS results in 95 - 99% oxidation of the sulfide and 70 - 85% conversion of the Fe²⁺ to Fe³⁺ within 20 minutes (Figure 6). Similarly, a 1.0 – 2.0 stoichiometric dose of NaOCl to the same wastewater results in 90 - 99% oxidation of the sulfide and 40 - 80% conversion of the Fe²⁺ to Fe³⁺ (Figure 7). It was also shown that there is no significant reaction between residual H₂O₂ (added to the influent sewers) and bleach (added before the clarifiers).

Figure 6. Beaker test results: H₂O₂ oxidation of sulfide and ferrous iron

Oxidant Dose ratio (x theoretical)	None Control	----- H ₂ O ₂ -----			
		1.0	2.0	3.0	4.0
Dissolved sulfide, mg/L	0.3	< 0.1	< 0.1	< 0.1	< 0.1
Total sulfide, mg/L	1.1	0.1	0.1	< 0.1	< 0.1
Total sulfide, % removal		91%	91%	> 91%	> 91%
Ferrous iron, mg/L	11.2	2.9	3.2	2.3	1.2
Ferric iron, mg/L	1.2	9.4	8.7	10.7	11.3
Ferric iron, % of total	10%	76%	73%	82%	90%

- NOTES:
1. Tests run in wastewater (20 mins reaction time)
 2. Dose ratio = Combined weight of total sulfide and ferrous iron
 3. Theoretical demand: (TS * 1.0) + (Fe²⁺ * 0.3)

Figure 6 (above) shows that for this sample, the 1.0 theoretical H₂O₂ demand equates to 4.5 mg/L, which removed virtually all the sulfide and converted ca. 70% of the Fe²⁺. Other tests substantiated the selectivity toward sulfide oxidation over Fe²⁺ oxidation and the practical H₂O₂

requirement of 1.5 – 2.5 times theory. It was also found that efficiencies degraded with low H₂O₂ doses (i.e., < 3-4 mg/L).

Figure 7. Beaker test results: Bleach oxidation of sulfide and ferrous iron

Oxidant	None	----- NaOCl -----			
Dose ratio (x theoretical)	Control	1.8	3.6	5.4	7.2
Dissolved sulfide, mg/L					
Total sulfide, mg/L	7.2	0.5	< 0.1	< 0.1	< 0.1
Total sulfide, % removal		93%	> 98%	> 98%	> 98%
Ferrous iron, mg/L	7.4	5.4	1.4	1	1
Ferric iron, mg/L	0.2	1.5	5.6	5.9	5.9
Ferric iron, % of total	3%	22%	80%	86%	86%

- NOTES:
1. Tests run in wastewater spiked with sulfide (20 mins reaction time)
 2. Dose ratio = Combined weight of total sulfide and ferrous iron
 3. Theoretical demand: (TS * 2.34) + (Fe²⁺ * 0.66)

Similar results were seen when using bleach as the oxidant. For this sample (spiked with sulfide), the 1.0 theoretical bleach demand equates to 21 mg/L, consistent with the active oxidant being monochloramine. A 1.8x theoretical dose (38 mg/L) removed 93% of the sulfide and converted ca. 20% of the Fe²⁺. A 3.6x theoretical dose converted 80% of the Fe²⁺. Hence, like H₂O₂, bleach required 2-3x the theoretical demand to convert 80% of the Fe²⁺ to Fe³⁺.

Jar tests

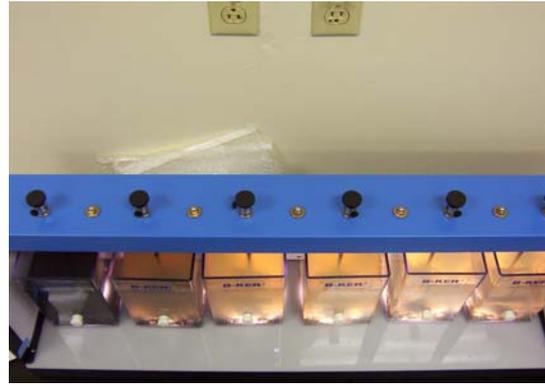
Jar testing was done to assess the effects of the different chemical doses on CEPT performance. Wastewater samples were spiked to provide a range of influent conditions (sulfide and ferrous iron levels) while varying the doses of H₂O₂, FeCl₃, and polymer, and measuring the resultant TSS and turbidity levels. Except where bleach was examined as the oxidant, the bleach dose was held constant at the amount typically needed to provide a residual (26 mg/L). The jar test series in Figure 8 (below) is one of ca. 30 such runs that looked at these effects against varying levels of influent sulfide and Fe²⁺.

Figure 8. Sample run of jar tests (showing impact of influent sulfide)

Sample: Miller-Holder interceptor

Parms: T.Sulfide... 10.5 mg/L (spiked from 0.7 mg/L)
 T. Iron 6.65 mg/L
 Fe2+ 5.98 mg/L

Chemical dose, mg/L	Stir rate (rpm)	Duration (mins)	---- Test Sample ----						
			1 Baseline (per plant)	2	3	4	5	6	
H2O2	1.0 = theory	40	20	0.0	0.5	0.8	1.0	2.0	3.0
FeCl3	mg/L Fe	60	2	7.0	3.5	3.5	3.5	3.5	3.5
Bleach	mg/L	60	2	26	26	26	26	26	26
Polymer	mg/L	100-5-0	3-45-15	0.15	0.15	0.15	0.15	0.15	0.15
Turbidity	FAU			159	158	126	114	74	66
Color	1 = best			6	5	3	4	2	1
TSS	mg/L			48	45	31	40	27	20



The particular series shown in Figure 8 is with high influent sulfide levels and moderate Fe²⁺ levels (nonetheless sufficient for CEPT). The first jar shows that 26 mg/L bleach was insufficient to completely remove the influent sulfide (theoretical demand = 28 mg/L), leaving the characteristic black FeS precipitate. Jars 2-6 show what happens when FeCl₃ doses (for CEPT) were cut in half while H₂O₂ dose (into the influent sewer) was increased from 0.5 to 3.0 times theory. The results show the complete removal of sulfide (as black FeS) at near theoretical H₂O₂ doses, though Fe²⁺ oxidation (as evidenced by lower TSS levels) required a 2-3 fold excess of H₂O₂. These results were predicted from the beaker tests (Figure 7).

Figure 9. Summary of jar test results

Influent Parameters		None		Oxidant H2O2 + Bleach		Bleach	
Sulfide	Ferrous	TSS	Turbidity	TSS	Turbidity	TSS	Turbidity
Low	Low	37 - 40	60 - 65	32	60	40 - 45	70 - 78
Low	High	33	20	25	44	38	45
High	Low	140 - 143	279 - 288	32	60	57 - 67	121 - 126
High	High	73	134	18 - 30	7 - 50	27 - 45	32 - 87

Sulfide: Low = < 1 mg/L ; High = 3 - 6 mg/L. Ferrous: Low = < 1, High = 4 - 8 mg/L
TSS values expressed as mg/L, Turbidity expressed as FAU (Hach).
Standard doses: 28 mg/L FeCl₃ and 0.15 mg/L polymer
H₂O₂ dosed at 1.0 stoichiometry; Bleach dosed at 26 mg/L

Figure 9 (above) summarizes the results of the 30 jar test series (180 tests). The data show that the effluent TSS and turbidity levels were heavily influenced by the levels of influent sulfide and iron, and thus the amount of oxidant added to react with these substances. High sulfide levels had a strong inhibitory effect (scavenging Fe³⁺ added for CEPT) with the resultant FeS precipitate blackening the water and increasing TSS and turbidity levels. Oxidizing the influent sulfide with H₂O₂ and/or bleach removed its inhibitory effect and thus preserved FeCl₃ for CEPT. High influent iron levels show an enhancing effect, particularly when H₂O₂ and/or bleach are added to convert the influent Fe²⁺ to Fe³⁺. The generally high turbidity levels associated with bleach but not H₂O₂ are attributed to bleach-polymer interactions that produce a murky/cloudy suspension that clarifies only slightly after prolonged quiescence (e.g., overnight). This murkiness/cloudiness is likely related to high settleable solids values. It was found that increasing Fe³⁺ levels (from 2 mg/L to 20 mg/L) and decreasing polymer levels (from 0.4 mg/L to 0.05 mg/L) improved the settleable solids values.

The results generally show that the oxidized influent Fe is as effective in CEPT as is freshly added FeCl₃. Thus, the additional Fe³⁺ produced by pre-oxidation may be used either to provide lower TSS values or to conserve FeCl₃ use. The most cost-effective scenario indicated by these jar tests was to use H₂O₂ both to remove the influent sulfide and to oxidize the influent Fe²⁺; though using bleach to oxidize the influent Fe²⁺ was also cost-effective provided the influent sulfide levels were low.

Field tests

The final stage of the evaluation consisted of plant tests to assess the practical efficiencies of implementing the lab guidance. The first order was to identify the levels of sulfide, TSS and settleable solids historically obtained (prior to PRI-SCTM or bleach, but with H₂O₂ injection into the influent sewers). These values are reported in the first column of Figure 10 (below). The second column reflects PRI-SCTM treatment within the collection system but no H₂O₂ or bleach addition at the treatment plant. This scenario occurs routinely since bleach is not added to those clarifiers that undergo secondary treatment (i.e., the A-side clarifiers).

Figure 10. Summary of results for plant tests: Historical and without bleach

		Historical			PRI-SC in Collection System		
		Primary Clarifier			Primary Clarifier		
		Grit Basin	Influent	Effluent	Grit Basin	Influent	Effluent
Sulfide	Total, mg/L	0.5	0.2	0.2	0.5	0.2	0.2
	Dissolved, mg/L	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Iron	Ferrous, mg/L	0.3	0.3	0.3	2.8	2.8	2.8
	Ferric, mg/L	0.1	6.5	1.5	1.5	9.7	0.4
TSS, mg/L				60			55
Settleable solids, mg/L				0.3			0.3

- NOTES: 1. 'Historical' values are without FeCl₂ added in the collection system, with H₂O₂ pre-oxidation, and without bleach added for primary disinfection
2. The increase in iron levels at the primary clarifier influent is due to the FeCl₃ added for CEPT.

The results in Figure 10 show that, historically, only background levels of Fe were present in the influent wastewater, and sulfide levels were controlled by adding H₂O₂ into the influent sewers. Effluent from CEPT typically contained 55-60 mg/L TSS and 0.3 – 0.4 settleable solids (measured during peak flow). With the implementation of PRI-SC™, iron levels into the the clarifiers increased by ca. 50%, with ca. one-third of that additional iron being Fe³⁺. The ferrous iron remained through the grit basins and clarifiers, confirming the Fe²⁺ fraction to be non-settleable (adding no benefit to CEPT). However, TSS levels were improved (due to the increase in ferric iron contributed by PRI-SC™), and settleable solids levels were unchanged.

The next two scenarios are similar to Column-2 in Figure 10 but reflect using either H₂O₂ or bleach to oxidize the influent ferrous iron (Figure 11, below).

Figure 11. Summary of results for plant tests: H₂O₂ or bleach as the oxidant

		H ₂ O ₂ as Oxidant			Bleach as Oxidant		
		Primary Clarifier			Primary Clarifier		
		Grit Basin	Influent	Effluent	Grit Basin	Influent	Effluent
Sulfide	Total, mg/L	0.2	< 0.1	< 0.1	0.5	< 0.1	< 0.1
	Dissolved, mg/L	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Iron	Ferrous, mg/L	1.8	1.8	1.8	2.8	< 0.1	< 0.1
	Ferric, mg/L	2.5	10.7	0.4	1.5	12.5	0.4
TSS, mg/L				45			40
Settleable solids, mg/L				0.3			0.8

- NOTES: 1. Values are with FeCl₂ added in the collection system
2. H₂O₂ was added to the influent sewers; bleach was added to the primary influent.
3. The increase in iron levels at the primary clarifier influent is due to the FeCl₃ added for CEPT.

The first column show shows that: 1) H₂O₂ addition caused residual sulfide levels to quickly go to below detection limits (reducing fugitive emissions through the headworks); and 2) a significant portion of the influent Fe²⁺ was oxidized to Fe³⁺. Again, unconverted Fe²⁺ passed through the clarifiers, and primary effluent TSS levels were lowered as a result of that portion of the contributed iron oxidized to ferric. Using bleach as the oxidant (Column-2, Figure 11) meant first that much of the complexed sulfide (0.5 – 2.5 mg/L) and all of the Fe²⁺ passed through the grit basins. However, both were oxidized to > 95% upon bleach addition, resulting full recovery of the iron contributed from PRI-SCTM. Primary effluent TSS levels were lowered still further as a result of the higher iron recovery, though settleable solids levels increased.

Analysis of plant records

The study also attempted to correlate historical chemical feed rates to CEPT performance records maintained in the plant database. This effort provided insight into the impact on TSS levels of iron contributed by PRI-SCTM. The plant process records show an association between lower TSS levels and higher iron dosing from PRI-SC. Also, plant sampling results showed that the Fe²⁺ contributed by PRI-SCTM is oxidized to Fe³⁺ upon bleach addition. Combined, this information was evidence that the Fe contributed by PRI-SCTM, once oxidized, enhances CEPT performance.

DISCUSSION

While this study showed that the ferrous iron added within the collection system for sulfide control can be oxidized to ferric iron that contributes to CEPT, it also highlights some shortcomings that may limit the utility. Most notable is the excess oxidant needed to drive the conversion of ferrous to ferric. For example, the results show that:

- 1) The dose ratios of oxidant-to-ferrous iron needed to push the recovery to > 80% are 2-3 times those predicted by theory;
- 2) The required dose ratio of oxidant-to-ferrous iron increases as the absolute level of Fe²⁺ decreases (e.g., to < 3-5 mg/L);
- 3) Adequate mixing of the oxidant into the wastewater is needed to minimize contact times and limit oxidant decay / loss.

With regard to the particular operational set-up at OCS D Plant No. 2, these shortcomings impacted H₂O₂ much more than bleach. For example, low total sulfide levels in the influent water meant that theoretical H₂O₂ demands were oftentimes < 2 mg/L; on the other hand, bleach is dosed to provide a residual AvCl (typically 26-30 mg/L) regardless of the levels of Fe²⁺ and sulfide. As a result, bleach demands attributable to Fe²⁺ oxidation were essentially 100% efficient even at 10x the theoretical dose. In contrast, Fe²⁺ conversions using H₂O₂ were inconsistent, varying from 10% to 80%. These relative conditions are unique to OCS D Plant No. 2 operations and, in most other situations, H₂O₂ would be the more cost-effective oxidant.

The utility of the regenerated (oxidized) iron is not limited to CEPT. For example, ferric iron is substantially more effective than ferrous iron at complexing phosphate (for nutrient removal). Also, as this study has shown, uncomplexed ferrous iron passes through the clarifiers and so does

not accumulate in the primary solids where it can subsequently control H₂S (or struvite) in digesters. Pre-oxidizing ferrous iron in the influent wastewater can thus provide benefit regardless of CEPT.

Another application of oxidant-regenerated ferrous iron is in solids conditioning / dewatering, i.e., prior to dewatering, oxidizing Fe²⁺ (either dissolved or as FeS) present in digested solids. The benefits would be similar to those realized at the front of the plant: improved odor control, enhanced coagulation / dewatering, and phosphate removal (from the filtrate).

CONCLUSIONS

This study has shown that it is cost-effective to add H₂O₂ (or bleach) to supplement those programs that use iron salts for sulfide control and enhanced clarification. The combination of FeCl₂ and H₂O₂ as employed in the PRI-SCTM / PRI-CEPTTM technology can afford improved performance and lower iron consumption, while providing economic benefit. It was shown that > 95% of the iron added within the collection system (for sulfide control) can be regenerated at the treatment plant for enhanced clarification purposes. The cost for oxidizing the influent Fe²⁺ in this study (to provide Fe³⁺) was ca. 40% less than the purchase price of FeCl₃. Hence, large municipalities that currently use iron salts for these purposes may find the results helpful in improving operations and hedging iron costs.

Nonetheless, the axiom 'every plant is different' applies to this study, and highlights that the iron regeneration technology must be adapted to each facility. The most cost-effective solution for OCS D Plant No. 2 involved using both H₂O₂ and bleach to affect the regeneration of Fe²⁺: H₂O₂ added to the influent sewers in amounts sufficient to oxidize sulfide; and allowing the Fe²⁺ to be oxidized as result of maintaining bleach residuals through the clarification process.

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