Cost Savings and Performance Improvement of Large System Iron Salt Use for Integrated Sulfide Control and Chemically Enhanced Primary Treatment by Using Peroxide Regenerated Iron Technology

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ABSTRACT

San Diego's Point Loma WWTP is a 160 MGD (240 MGD permitted), 100% advanced primary treatment plant that has historically used iron salts for collection system sulfide control and chemically enhanced primary treatment. Beginning in 2006, a PRI-SC® (Peroxide Regenerated Iron – Sulfide Control) program was implemented by adding H_2O_2 at the intermediate pump station PS2 (in place of the $FeCl_3$), and again to the plant influent (ahead of $FeCl_3$ addition for CEPT). The application of PRI-SC® in the Point Loma system was designed to provide at least $685/day in cost savings, to be achieved through reduced ferric chloride use at PS2 and Point Loma, while improving sulfide control and CEPT performance. Since integrating the PRI-SC® program full-time in 2008, SDMWD is realizing savings of approximately $4,700 per day (~$1.72 million/yr) compared to the 2007 baseline iron salts program. At the same time, both sulfide control and CEPT performance has improved. The cost savings were helped by the hedging aspect of the PRI-SC® program – iron salt price volatility in 2008 and 2009 was upwards of 45%. The PRI program has reduced the total iron salt use from the 2007 baseline rate of 32.5 dry tons per day to approximately 19.3 dry tons per day in 2009, with the core savings coming from an overall reduction in ferric chloride use at PS2 and the treatment plant (Table 1). Significantly, ferric chloride use at PS2 was eliminated and, for CEPT, it was reduced from 24 mg/L to 10 mg/L (16.6 to 6.8 dry tons per day) with no loss in performance. In addition, total sulfide removal has improved over baseline levels, and average CEPT performance exceeds the permit levels at 89% for TSS and 65% for BOD, and effluent water quality has improved (with 60% less spent iron (as FeS) present in the ocean discharge). For the most part, digester biogas H_2S levels were maintained below the permit requirement of < 40 ppm, but required approximately twice the baseline $FeCl_2$ feed rate. Even so, the overall program has maintained the stated savings benefit.

KEYWORDS: Sulfide control, iron salts, Chemically Enhanced Primary Treatment (CEPT), hydrogen peroxide, PRI-SC, Peroxide Regenerated Iron.

INTRODUCTION

The metropolitan sewerage system of greater San Diego serves a population of 2.2 million people from 16 cities and districts, generating approximately 180 million gallons of wastewater per day. Planned improvements will increase treatment capacity to 340 million gallons per day by 2050 to serve an estimated 2.9 million people. San Diego's Public Utilities Department, Wastewater Treatment and Disposal Division (WWTD) provides wastewater treatment services for this 450 square mile service area, which includes the City of San Diego's collection system and the Point Loma Wastewater Treatment Plant (Point Loma WWTP).

Approximately 60 MGD of the wastewater collected in the City of San Diego are conveyed through Pump Station 1 (PS 1), which subsequently combines with an additional 100 MGD of flow at Pump Station 2 (PS 2). From here, PS 2 delivers wastewater to the Point Loma WWTP.

Figure 1: Aerial View of the Point Loma Wastewater Treatment Plant

San Diego's Point Loma WWTP (**Figure 1**) is a 100% advanced primary treatment plant and the only remaining facility in the United States that maintains a 301(h) modified permit for effluent discharge (a "secondary treatment waiver"). The Point Loma facility treats approximately 160 MGD of wastewater utilizing "Chemically Enhanced Primary Treatment" (CEPT) to lower BOD and TSS to levels acceptable for deep ocean discharge. In the CEPT process, ferric chloride ($FeCl_3$) and anionic polymer are added to the plant's influent flow prior to the primary clarifiers to "enhance" flocculation and reduce BOD and TSS levels. Point Loma's discharge permit requires removal rates of TSS and BOD of 80% and 58% respectively, though staff operational goals are 89% and 65% to ensure year-round permit compliance.

Historically, iron salts have been used by WWTD since the 1960's, but did not become an integral part of the treatment process at Point Loma until the 1990's. At that time, $FeCl_3$ was used for both odor control in the collection system and settling enhancement at the WWTP. In the late 1990's, WWTD began investigating whether better system performance could be achieved by applying ferrous chloride at some sites and ferric chloride at others. Through significant study, it was determined that this combination approach to iron salt application offered both cost and treatment efficiency improvements over the original ferric only strategy.

Beginning in 1998, WWTD first piloted its "Bid to Goal" (B2G) initiative to improve efficiency and effectiveness throughout all its operations, with an initial goal to reduce the WWTD budget by $77 million through 2004. To achieve this five-year target, WWTD targeted $20 million per year in operational savings. The B2G process challenges each WWTD department, through annual bidding of improvements to be achieved through process or operational means, to meet a goal that represents a portion of the total WWTD target savings for the year. Due to its success in the first five years, B2G was extended in 2005 for four more years, which included Business Process Re-Engineering (BPR) in 2006 and implementation of “Most Efficient Organization” (MEO) in 2007.

As part of these changes, WWTD staff was reduced from a planned 330 people in 1998 to 281 people in 2010. At Point Loma, Process Control Staff was reduced from four employees (senior supervisor, supervisor, and two operators) to one supervisor, while additional responsibilities were added to the group as other groups were also downsized.

In addition to staff reductions, chemical budgets were also targeted for optimization. While Point Loma’s iron program was an integral part of the advanced treatment process, it also represented the largest chemical budget in all of WWTD. To complicate this issue, iron expenditures have expanded rapidly from 2004 through 2009. **Figure 2** demonstrates the sharp uptrend in San Diego’s iron unit pricing, which was the primary driving force for Point Loma to seek out PRI-SC® as an alternative technology.

PRI-SC® was first briefly trialed in the summer/fall of 2006 at a proof-of-concept level with results indicating that the process had potential to achieve future cost savings for Point Loma, however, a second longer term evaluation was required. Following the PRI-SC® trial in 2006, Point Loma staff achieved B2G savings through further optimization of their iron-only treatment program, which provided a firm baseline for comparing to a future longer-term PRI-SC® study. In 2008, WWTD’s Bid to Goal required a department-wide chemical budget reduction of 10%. As part of this initiative, Point Loma chose to re-implement PRI-SC® with an initial minimum target savings of $685/day over the 2007 iron-only baseline.

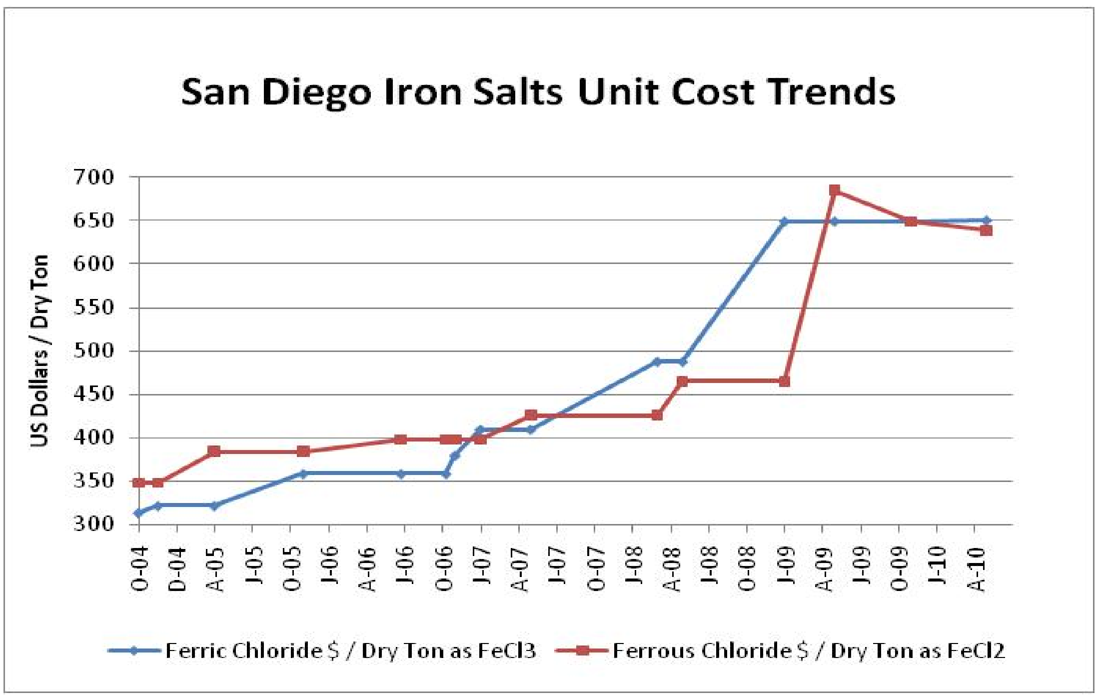

Figure 2: San Diego Iron Salts Unit Cost Trends

APPROACH / METHODOLOGY

Conceptually, the Peroxide Regenerated Iron technologies (PRI-TECH™) harness the natural propensity for ferrous sulfide (FeS) to air-oxidize in gravity sewers (Nielsen, et.al., 2005 and Firer, et.al., 2008), and is applicable anywhere that iron is fed for treatment of sulfide, whether sulfide control is the primary goal (Walton, et.al., 2003), or where competing side reactions are problematic as with $FeCl_3$ added for enhanced primary clarification (Walton, et.al., 2005) or for Chemical P-removal (Neofotistos, et.al., 2010). For the initial project at Point Loma, the PRI-SC® and PRI-CEPT™ technologies (PRI program) provided the best opportunity for process optimization and savings consistent with San Diego's B2G objectives.

The PRI-SC® process, depicted in **Figure 3**, is a patented technology that combines the use of iron salts and hydrogen peroxide (H_2O_2) in a unique fashion, whereby an iron salt is added in the upper reaches of the collection system (as the primary sulfide control agent) and H_2O_2 is added at specific points downstream (to "regenerate" the spent iron, FeS). The regeneration step oxidizes the sulfide to elemental sulfur and in the process "frees up" the iron for subsequent sulfide control downstream in the system. The PRI-SC® technology is being applied for sulfide control in collection systems at several major utilities throughout the country

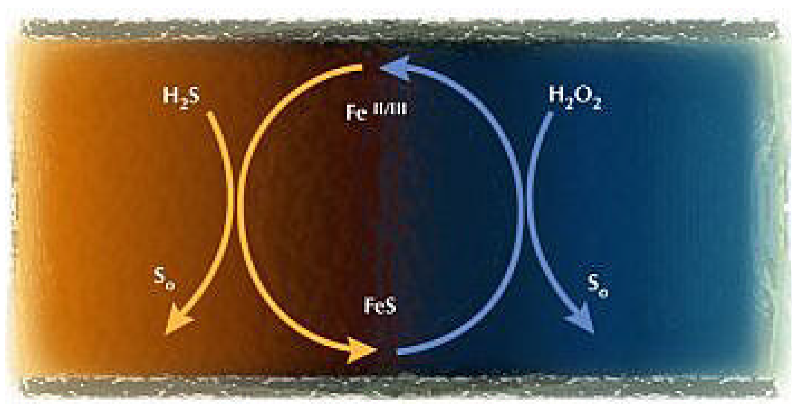

Figure 3: PRI-SC® Iron Regeneration Cycle

Integrating the PRI strategy with the treatment plant operations can be achieved by the proper placement of a final regeneration step (H_2O_2 addition) in front of the treatment plant to remove influent total sulfide that would otherwise interfere with the application of $FeCl_3$ for CEPT (PRI-CEPT™) and or phosphorus removal. Sulfide, whether in dissolved form or bound with iron as FeS, directly competes for ferric iron that is added for flocculation. In both of these forms sulfide reduces the ferric iron (Fe^{+3}) to ferrous (Fe^{+2}), which does not readily flocculate with anionic polymer, and is therefore not effective for CEPT. By preemptively oxidizing both total and dissolved sulfide with H_2O_2 prior to $FeCl_3$ addition, this competition for ferric is avoided with a net result being enhanced treatment performance at a greatly reduced cost.

Figure 4 depicts the Point Loma collection system and treatment plant sections relative to the application layout of the PRI program and the respective chemical feed locations. In practice, $FeCl_2$ is fed at PS 1 under both the Fe-only and PRI program scenarios (in the same amounts) to eliminate odor complaints between PS 1 and PS 2. As essentially all of the Fe from PS 1 arrives at PS 2 as FeS (spent) along with some dissolved sulfide, the PRI technology calls for H_2O_2 addition at PS 2 in an amount sufficient to oxidize both the dissolved and bound sulfide (FeS). The H_2O_2 feed point at the headworks of the Point Loma WWTP serves a similar purpose and thereby eliminates the background $FeCl_3$ demand (fed subsequently for advanced primary treatment) due to sulfide. In summary, relative to the iron-only approach, the PRI program approach is to:

1) Maintain current $FeCl_2$ feed rates at PS 1;

2) Substitute H_2O_2 for $FeCl_3$ at PS 2; and

3) Substitute H_2O_2 for (partial) $FeCl_3$ replacement at Pt. Loma (for CEPT).

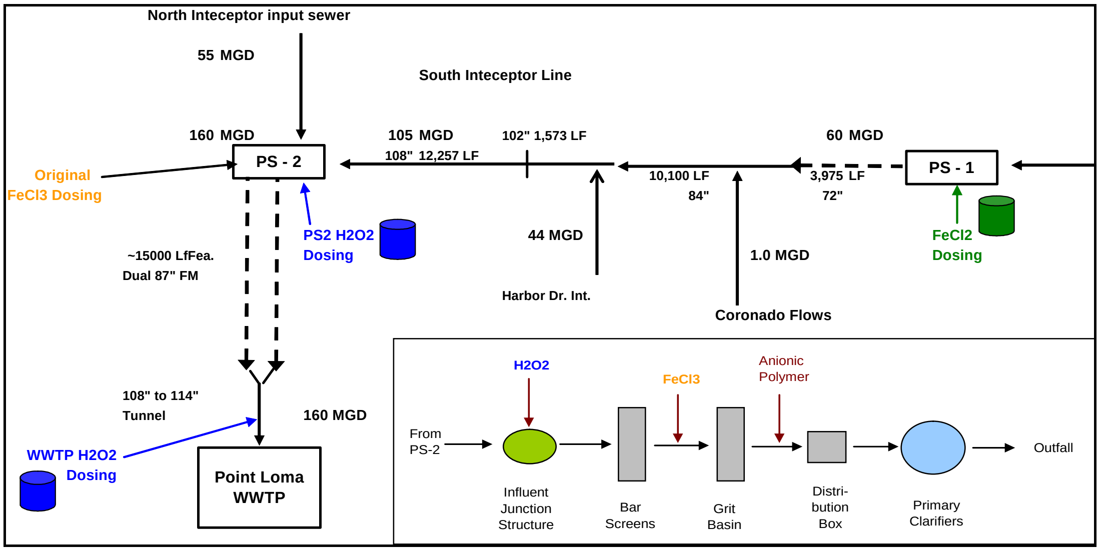

Figure 4: Point Loma PRI Program / Application Layout

Ultimately, the regeneration/recycling of iron with H_2O_2 in the wastewater treatment process offered multiple opportunities for efficiency gain in San Diego, with minimal capital, operational or personnel impact**,** which was the primary driver for the B2G program. Within the context of this program, the PRI technologies offered:

1. Economic fit - for Point Loma, PRI-SC® made economic sense and supported key B2G objectives – it offered a process solution that could quickly reduce the iron salts budget by >10% with negligible capital outlay. Additionally, regenerating iron with H_2O_2 provided a critical hedge against iron price inflation through reducing the total amount of iron used. Having multiple treatment chemicals provided increased flexibility to adjust to changing market forces.

2. Technical/Process fit - from a technical point of view, the value of additional flexibility in process control offered by the PRI-TECH™ approach is considerable. This flexibility manifests as different 'levers' the plant may use to quickly address changes in Fe and H2O2 pricing, short-term treatment performance, and influent sulfide loading, and in so doing, complement treatment strategies to overcome limitations of infrastructure or

operations. Indeed, if well implemented, management and optimization of the PRI chemical feed strategies can offer the potential of greatly improving the performance of treatment without disrupting the more rigid structures of day-to-day operations in a collection system or treatment plant.

<u>Sampling locations</u>		
	Collection system	PS-1 influent
		PS-2 influents
	Treatment plant	Influent junction structure
		Bar screens
		Headworks odor scrubber inlet
		Primary clarifier distribution box
		Primary effluent
		Primary settled solids
		Digester biogas
<u>Sampling frequency</u>		
	Liquid sampling	Grab samples collected 4-8 times daily, Monday - Friday
		Periodic 24-hourly grab samples
	Vapor sampling	Continuous datalog (24/7)
<u>Liquid analyses</u>		
	Total sulfide	Std. Methods 4500-S^{2-} D. Methylene Blue (Lamotte drop count kit)
	Dissolved sulfide	Ditto, using pre-flocculation to remove insoluble sulfides
	pH	Narrow range pH test strips (+/1 0.2 units)
	Temperature	NIST calibrated thermometer
	Total iron	Std. Methods 3500-Fe D. Phenanthroline (Hach colorimeter)
	Ferrous iron	Ditto, using mild acidification and heating to dissolciate FeS
	Residual H2O2	Enzymatic redox test strips (e.g., EM Quant)
	TSS	Std. Methods 2540 D. TSS dried at 103-105 deg-C
	BOD	Std. Methods 5210 B. 5-Day Demand
<u>Vapor analysis</u>		
	H2S	App-Tek OdaLog (Detection Instruments)

Figure 5: Sampling Locations, Frequency, and Methods

Other potential technical benefits that made the choice of PRI significant include:

- Improved odor control – Fe-catalyzed H_2O_2 is more efficient than Fe for driving dissolved sulfide to very low levels;
- Reduced sulfide loads to downstream processes (CEPT, scrubbers, etc.);
- Lower environmental impact at the ocean outfall and reduced volume of solids delivered to the landfill - due to reduced overall iron usage;
- Improved settling/treatment is possible; and
- Improved effluent quality in terms of appearance and bleach demand for disinfection.

Finally, because PRI-SC® was offered by US Peroxide as a full-service application, Point Loma was able to implement it with minimal strain on labor. US Peroxide maintains ownership and responsibility for the H_2O_2 dosing systems (**Figure 6**), which eliminates the need for maintenance and upkeep by Point Loma and minimizes staff exposure to H_2O_2, which has very specific handling intricacies. Furthermore, US Peroxide staff was able to step in to monitor and optimize the PRI-SC®/PRI-CEPT™ process in conjunction with the reduced Process Control staff at Point Loma.

Figure 6: Headworks Hydrogen Peroxide Feed System

RESULTS

The results from the Proof-of-Concept test in 2006 showed the PRI program to be a cost-effective way to enhance iron efficiency (**Table 1**, below). The conclusions of this early test were:

1. The PRI program demonstrated improved sulfide control while maintaining the TSS and BOD removal rates at acceptable levels (88% and 60%, respectively); and

2. The projected cost savings afforded by PRI was approximately $650,000 annually (or 11%).

Table 1: Proof-of-Concept Test Results Comparing the PRI program to Iron-Only

	Baseline (FeClx only)	PRI-SC
Chemical feed rate totals, gpd		
Iron salts (FeCl2-35% + FeCl3-42%)	15,080	8,020
Hydrogen peroxide (50%)	0	2,100
Liquid sulfide, mg/L (Total / Dissolved)		
Influent to Pt. Loma plant	2.5 / 0.3	0.6 / 0.1
After FeCl3 addition for CEPT	2.1 / 0.1	0.3 / < 0.1
Primary effluent	0.7 / 0.1	0.1 / < 0.1
Primary effluent, % removals		
TSS	87%	88%
BOD	62%	60%
Chemical costs, $K per year		
Iron salts	5,724	3,044
H2O2	0	2,031
	-------------	-------------
Total	5,724	5,076
Difference	649	
	11%	

Table 1 Note: All costs exclude FeCl2 added to anaerobic digesters.

Following the 2006 proof-of-concept demo, WWTD initiated a 15-month optimization period of its iron-only treatment process in order to establish a sound baseline of cost and performance to compare against a future long-term PRI program. This optimization period continued through the end of 2007.

Long-term application of the PRI program began in January of 2008. Utilizing the findings from the proof of concept demo, as well as the subsequent iron-only baseline period in 2007, initial feed rates were chosen for all iron and peroxide feed sites, and optimization progressed according to downstream demand. Once sulfide was controlled in the collection system, the strategy for optimization was to continue to maintain treatment standards upstream while slowly reducing the $FeCl_3$ feed target at the WWTP without sacrificing treatment performance of TSS and BOD removals for CEPT.

$FeCl_3$ feed reductions continued through July of 2009, though March 2009 data is used here to represent optimized feed rates since a PRI study on the WWTP's primary sludge began in April of 2009 (which interfered with later results). Shown in **Table 2** below are the initial and optimized feed rates for the 2008 PRI program along with 2007 baseline iron feed rates.

Table 2: PRI Program Optimization - Chemical Feed Rates (Average Gallons per Day)

	PS 1	PS 2		PLWWTP			Totals		
	$FeCl_2$	$FeCl_3$	H_2O_2	H_2O_2	$FeCl_3$	$FeCl_2$	$FeCl_2$	$FeCl_3$	H_2O_2
2007 Fe Program (Annual Average)	4035	2314	0	0	6939	1344	5379	9252	0
PRI-SC Startup (January 2008)	3991	0	720	461	7675	1435	5426	7675	1181
PRI-SC Optimized (March 2009)	4212	0	897	637	3010	2019	6231	3010	1534

Table 3: PRI-SC® Program / Treatment Performance

Treatment Parameter	Daily Averages 2007 Fe Alone	2008 PRI Program	2009 PRI Program	Minimum Permit Target
TSS Removal (%)	89.1	88.2	89.6	>80%
BOD Removal (%)	68.5	65.5	65.4	>58%
Effluent Fe (mg/L)	6.2	2.7	2.3	N/A

Table 4: Aqueous Sulfide Treatment Results

	Point Loma Influent		Primary Clarifier Influent		Primary Clarifier Effluent	
	Total S^{-2} (mg/L)	Dissolved S^{-2} (mg/L)	Total S^{-2} (mg/L)	Dissolved S^{-2} (mg/L)	Total S^{-2} (mg/L)	Dissolved S^{-2} (mg/L)
2007 Baseline(Annual Average)	1.6	0.2	0.9	< 0.1	0.3	< 0.1
2008 PRI-SC Program	1.7	0.4	0.6	0.1	0.1	< 0.1
2009 PRI-SC Program	1.4	0.5	0.9	0.3	0.1	< 0.1

Throughout this optimization period, treatment results remained consistent and well within the target levels. Due to reduced iron particulate levels in the plant effluent, TSS removal was improved with PRI, though BOD removal decreased slightly but still within permit targets. **Tables 3 and 4** above summarize the average WWTP performance achieved through the optimization period. However, the impact of optimization through 2008 and 2009 is best demonstrated through the cost savings achieved by the PRI program shown in **Table 5**.

DISCUSSION

As of November 2009, the Point Loma PRI program was achieving $4740/day in savings over the 2007 baseline, with most of the savings realized through the optimization of $FeCl_3$ feed at the WWTP. Based on current pricing, **Table 6** details the savings rate achieved by the PRI program during the first half of 2010. Although current savings rates are slightly lower than 2009, they greatly exceed the initial target of $685 per day. The largest portion of the savings was generated by the reduction in $FeCl_3$ use for CEPT and the elimination of $FeCl_3$ use at PS 2. Total $FeCl_3$ use was reduced by 69% from 2007 to 2009.

Table 5: 2009 PRI Program / Iron Salts and H_2O_2 Cost Reduction Results

Chemical	Current Chemical Unit Cost	City Fe 2007 Program Basis		2009 PRI Program		Avg Daily Cost savings
		Avg Daily Use	Avg Daily Cost	Avg Daily Use	Avg Daily Cost	
FeCl3 PS2 (DT)	$695/DT	5.5	$3,823	0	$0	$3,823
FeCl3 PL (DT)	$695/DT	16.6	$11,537	6.8	$4,726	$6,811
FeCl2 PL (DT)	$649/DT	2.6	$1,687	5.2	$3,375	-$1,688
FeCl2 PS1 (DT)	$649/DT	7.8	$5,062	7.3	$4,738	$324
H2O2 - 50% PS2 (gal)	$2.99/gal	0	$0	885	$2,646	-$2,646
H2O2 - 50% PL (gal)	$2.99/gal	0	$0	630	$1,884	-$1,884
Total			**$22,109**		**$17,369**	**$4,740**
Note: pricing reflects current as of November 2009.						

Table 6: 2010 PRI Program Performance (Through 6/30/2010)

Chemical	Current Chemical Unit Cost	Fe 2007 Program Basis		2010 PRI Program		Avg Daily Cost savings
		Avg Daily Use	Avg Daily Cost	Avg Daily Use	Avg Daily Cost	
FeCl3 PS2 (DT)	$650/DT	5.5	$3,575	0	$0	$3,575
FeCl3 PL (DT)	$650/DT	16.6	$10,790	6.8	$4,420	$6,370
FeCl2 PL (DT)	$639/DT	2.6	$1,661	4.8	$3,067	-$1,406
FeCl2 PS1 (DT)	$639/DT	7.8	$4,984	8.5	$5,432	-$447
H2O2 - 50% PS2 (gal)	$2.99/gal	0	$0	893	$2,646	-$2,646
H2O2 - 50% PL (gal)	$2.99/gal	0	$0	614	$1,884	-$1,884
Total			**$21,011**		**$17,449**	**$3,562**
Note: pricing reflects current as of July 2010.						

The savings impact of $FeCl_3$ use reduction was further amplified by the sharp $FeCl_3$ pricing increase that Point Loma experienced over the same period (Figure 1). Because H_2O_2 pricing remained relatively stable over the same period, the PRI strategy acted as a hedge against rising iron prices. Ultimately, slight decreases in iron pricing since 2009 have reduced the daily savings rate slightly in 2010 to $3562/day or $1.2M/yr.

CEPT treatment performance remained consistent through PRI implementation (Table 3). TSS removal rates remained stable at approximately 89%. BOD removal rates were observed to decrease slightly through optimization, but continue to remain well above permit targets. Most significantly, a 63% decrease in $FeS_{(s)}$ in the treatment plant effluent was observed over the optimization period.

Reduced $FeS_{(s)}$ in the effluent has the added benefit of reducing the environmental impact of iron at the ocean outfall, and improving the subjective appearance of the effluent (lighter color). A more tangible impact of reducing effluent iron levels is the subsequent reduction in effluent bleach demand. Because the Point Loma WWTP was not required to implement partial effluent disinfection until 2008, no baseline bleach requirement was established, and thus the savings impact due to reduction in background $FeS_{(s)}$ bleach demand has not yet been determined but is likely significant

The PRI program has improved sulfide treatment at Point Loma overall, but inspection of the sulfide treatment results shows that sulfide levels increased slightly from 2008 to 2009 (Table 4). Although counterintuitive, this is a positive result in the context of improving CEPT performance over the same period. Indeed, as chemical usage decreased throughout optimization, sulfide concentrations would have necessarily increased. These slight increases indicate that neither H_2O_2 nor iron are being overfed in the process.

One side effect of the large iron reductions made during PRI-SC® optimization was an increased demand for iron to maintain biogas H_2S control in the anaerobic digesters. As iron feeds were reduced in the collection system and primary clarifiers, there arose a need to compensate by increasing $FeCl_2$ feed into the digesters (Table 2), implying that there is a minimum inventory of iron required to maintain the (air permit mandated) biogas H_2S target in the digesters. In 2009, a PRI-DE™ (Peroxide Regenerated Iron – Digester Enhancement) study was performed on the primary settled sludge that attempted to negate the increased iron demand by extending the PRI analogy into the plant primary solids. In this instance however, addition of extra ferrous chloride proved to be more efficient than the regeneration of spent iron in the sludge. This outcome is likely attributable to H_2O_2's propensity to decompose in high solids streams, particularly where dissolved sulfide levels are very low and iron concentrations are high (decomposition catalyst). Even with the increase in ferrous feed to the primary solids, the overall loading of iron to the digesters has decreased significantly, and it is likely that a reduction in finished solids output (and disposal costs) is also being realized by WWTD, although this has not yet been quantified.

CONCLUSIONS

The PRI program at the Point Loma WWTP has been highly successful in reducing process chemical costs and has greatly exceeded WWTD's initial 10% Bid to Goal target cost reduction. In addition, the ability of PRI to limit WWTD's exposure to large iron price fluctuations proved critical over the last two years, even though the ability to create a protective "hedge" against these price changes was not the primary driver for the initial trial. Furthermore, improvements in effluent quality played a crucial role in helping the treatment plant retain its secondary treatment waiver for another five years when their discharge permit came under review in 2009.

Within WWTD, continual improvement in both cost and operational efficiency meant that a higher wastewater treatment standard had to be achieved with less money and personnel. In this case, demands were subsequently met by implementing PRI in partnership with US Peroxide, who provided not only equipment and chemicals, but also technical implementation experience and permanent (dedicated) personnel for operations and optimization. The additional labor furnished by US Peroxide provided the capacity to experiment, investigate, and innovate where city resources are too limited to do so. Thus, ways to improve the treatment process beyond what is required by regulating agencies could be discovered. Some examples of projects that are planned or underway include:

- Point Loma PRI-DE™ (regeneration of FeS in the anaerobic digester sludge recirculation loop)
- Further improvement to $FeCl_2$ feed strategy at PS 1

- Optimization of H_2O_2 feed profiles at PS 2 and the WWTP headworks
- Profiled dosage of WWTP $FeCl_3$ utilizing continuous effluent TSS monitoring
- Additional applications at other WWTD facilities (NCWRP, MBC, GAPS, etc.)

Medium to large municipalities that currently use iron salts for controlling sulfide, phosphorus, and CEPT may find the experience of WWTD particularly helpful in improving operations and hedging iron costs. More practically, municipalities currently practicing these treatments may now find that they can fund enhancements to operations through existing budgets.

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