

**PEROXIDE REGENERATED IRON-SULFIDE CONTROL (PRI-SC)<sup>TM</sup>:  
INTEGRATING COLLECTION SYSTEM SULFIDE CONTROL WITH ENHANCED  
PRIMARY CLARIFICATION BY ADDING IRON SALTS AND HYDROGEN PEROXIDE**

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**ABSTRACT**

Iron salts are used by municipalities worldwide to control hydrogen sulfide within collection systems and to enhance primary clarification at treatment plants. However, the two uses are not synergistic: the product of the sulfide reaction is predominantly ferrous sulfide (e.g., FeS), a tightly-bound black precipitate that does not enhance flocculation. Further, dissolved sulfide present in the plant influent can scavenge free iron added to enhance clarification. Adding supplemental iron salt for both purposes would increase costs and potentially cause problems associated with e.g., higher volume solids production, reduced alkalinity, elevated salinity levels, and depleted dissolved oxygen. This paper presents the results of a field trial conducted at the Orange County Sanitation Districts using a novel technology to moderate these shortcomings – Peroxide Regenerated Iron – Sulfide Control (PRI-SC<sup>TM</sup>, patent pending). The combination treatment involves adding an iron salt at the upper reaches of the collection system and hydrogen peroxide at points downstream. The process may be viewed as an oxidant (H<sub>2</sub>O<sub>2</sub>) regenerating the spent iron salt (FeS) *in-situ* – yielding ferrous / ferric iron and colloidal sulfur. The study involved three major interceptors and the results show the PRI-SC technology met the control objectives at a significantly lower cost than other commonly used chemical technologies. Further, much of the ferrous salt added in the collection for sulfide control was shown to be converted to hydrous ferric oxide at the treatment plant for enhanced clarification purposes. OCSD has since extended the field test into a full year evaluation.

**KEYWORDS**

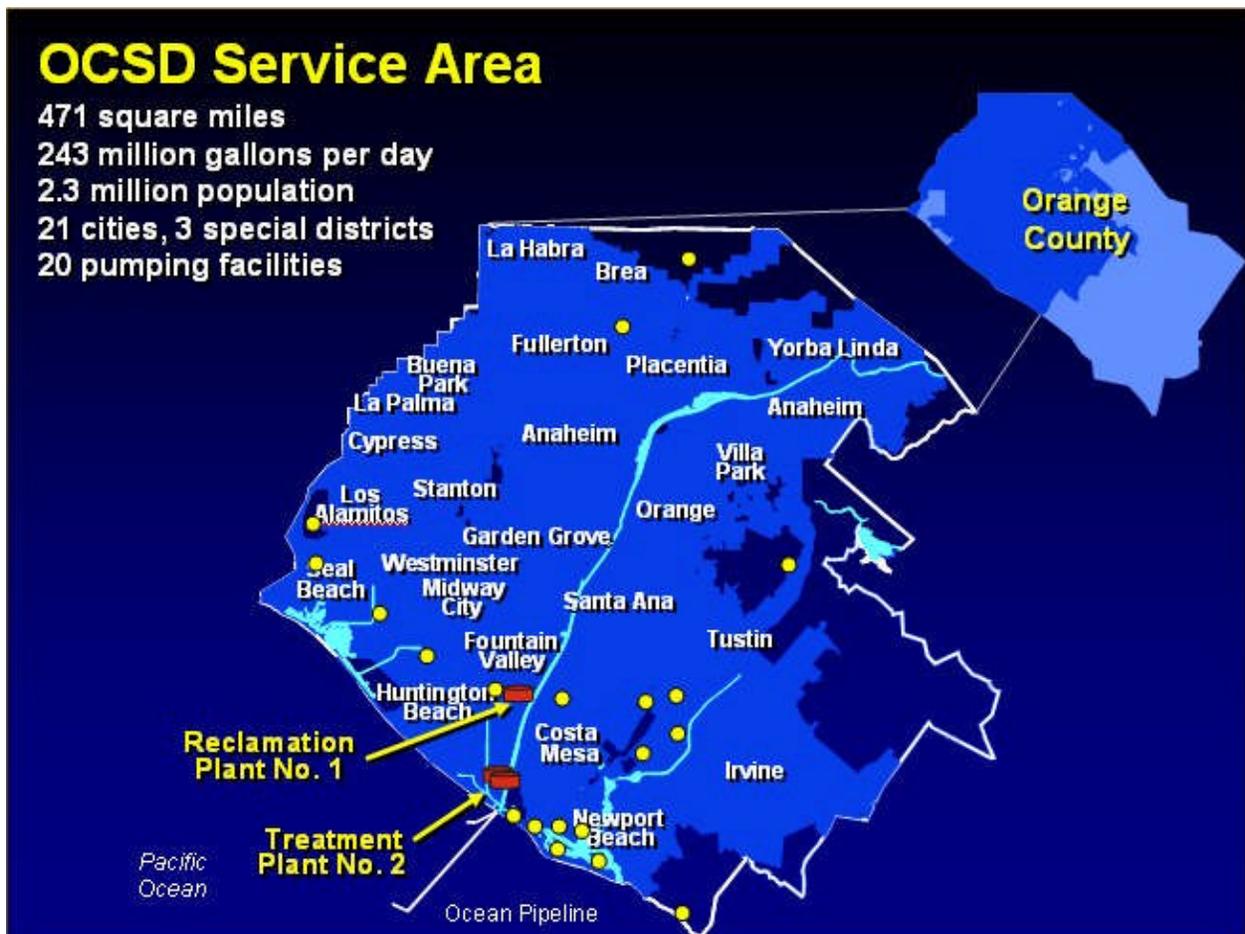
Hydrogen sulfide, odors and corrosion, iron salts, hydrogen peroxide, enhanced clarification

## INTRODUCTION

### Orange County Sanitation District

The Orange County Sanitation District (OCSD) operates approximately 380 miles of trunk sewers ranging in size from 12-inch to 96-inch diameter. This extensive system covers an area of approximately 470 square miles and serves a population of approximately 2.3 million people through twelve major, separate drainage basins. The collection system conveys wastewater generated by residential, commercial, and industrial sources from 21 cities. The wastewater is delivered to two treatment plants (80 mgd and 160 mgd, respectively) where it undergoes chemically-enhanced primary treatment and 50% secondary treatment, and is discharged to the ocean.

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



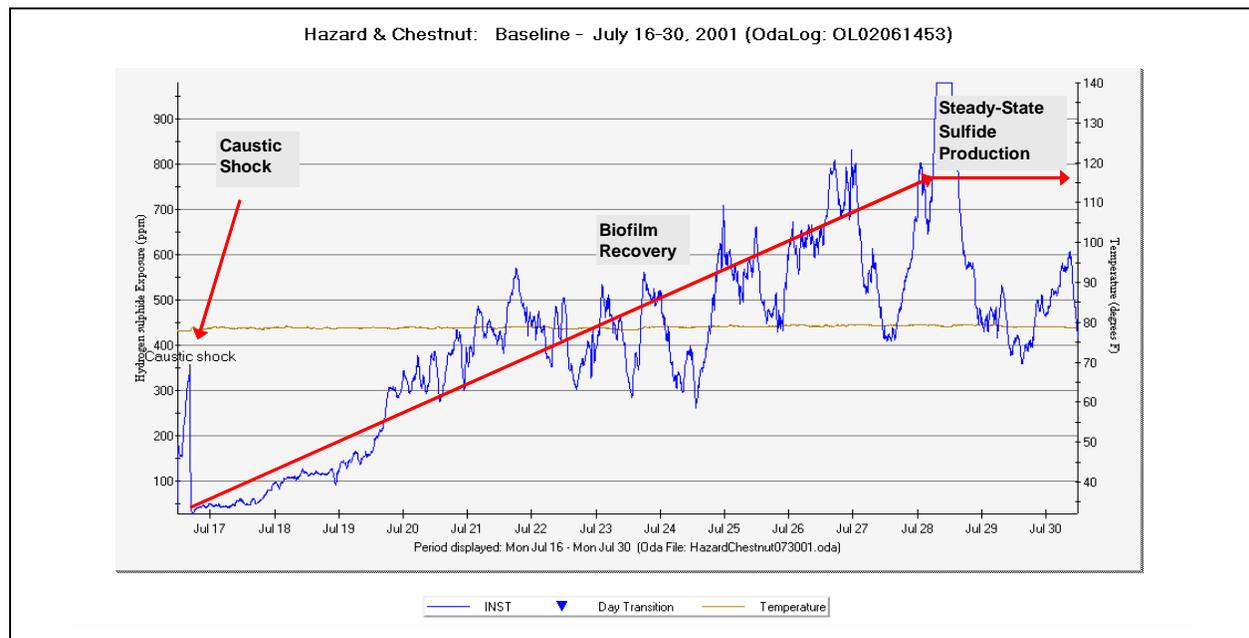
Since 1981, when OCSD's first odor control program was initiated, several projects have been implemented to reduce odors in its treatment plants and collection systems. These include covering the preliminary and primary wastewater treatment processes, collecting and scrubbing the foul air, adding chlorine and (later)  $H_2O_2$  to the influent trunklines, which help oxidize odor causing compounds, and installing mechanical contrivances to reduce wastewater turbulence. As a result, the number of odor

complaints received from the residents decreased from 125 to four or five per year for each of the plants over the last ten years.

In the mid-1980's, OCS D implemented advanced primary treatment (chemically-enhanced clarification) that involves adding of ferric chloride ( $\text{FeCl}_3$ ) and anionic polymer to the primary influent to obtain a clear effluent substantially free from colloidal and suspended matter. While the degree of clarification obtained depends on the quantity of chemicals used and the care with which the process is controlled, TSS removals were typically improved from 40-60% to 80-90%, and BOD removals were improved from 30-40% to 40-70%.

Odor control efforts specific to the collection system began in 1985 with a general odor abatement study. That study resulted in OCS D implementing in 1987 a sodium hydroxide (caustic) shock dosing program for two of the trunklines. This program was refined and expanded over the next 10 years to include nine trunklines. The caustic shocking program was revisited in 1997 and 1998 by two studies: collection system characterization and preliminary corrosion assessment. Among the findings was that biofilm recovery after a shocking incident (as evidenced by vapor  $\text{H}_2\text{S}$  levels) is rapid: partial recovery (33-50%) occurs within 1-2 days and complete recovery occurs within 3-4 days (Figure 2).

**Figure 2.  $\text{H}_2\text{S}$  recovery following a caustic shock**



Such rapid recovery results in inconsistent  $\text{H}_2\text{S}$  control within the collection system (which exacerbates odor complaints) and overfeeding of sulfide control chemicals at the treatment plants.

A follow-on study in 2000 looked more closely at the caustic shocking program in terms of its impact on treatment plant operations. Specifically, a correlation was observed between the high pH slugs entering the plants and elevated TSS and BOD levels in the

secondary effluent. As a result, a comprehensive Odor Characterization and Assessment Program was launched by the OCSD Air Quality and Special Project Division in the Operations and Maintenance Department. This effort was to address three primary concerns:

- Minimize odor complaints in the communities served by the trunklines;
- Optimize and integrate the odor control program in the collection system and the two treatment plants (provide for consistent control of sulfides);
- Reduce the potential for corrosion in the collection system.

A key component of the effort was to evaluate alternatives to caustic shock dosing within the collection system. In the Summer-Fall of 2000, following a comprehensive literature survey, field demonstrations of several single-chemical treatments were conducted on specific lines within the collection system. The chemicals evaluated were: calcium nitrate, sodium nitrate, hydrogen peroxide, magnesium hydroxide, and ferrous chloride. The control objectives were < 0.5 mg/L dissolved sulfide and < 25 ppm vapor H<sub>2</sub>S. The results indicated that two of the five chemicals (nitrates and magnesium hydroxide) performed very well in achieving headspace and/or liquid sulfide levels; however, the projected costs to apply these chemicals were several times that of the caustic shock dosing program, and so further study was begun.

The following year OCSD awarded a contract to US Peroxide to demonstrate a novel (patent pending) technology that uses an iron salt and H<sub>2</sub>O<sub>2</sub> to combine sulfide control within the collection system with enhanced primary clarification at the treatment plants, termed PRI-SC™ (Peroxide Regenerated Iron – Sulfide Control, patent pending). This paper presents the findings of the initial PRI-SC study which lasted August – December, 2001.

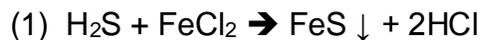
### **Industry experience**

Of the chemicals used by the wastewater industry to control sulfide, four find widespread use within collection systems: sodium hypochlorite, iron salts, hydrogen peroxide, and nitrates (calcium or sodium). Figure 3 (below) lists the comparative costs for using these chemicals. The wide variability in treatment costs reflects the unique aspects of each chemical that may be warranted for a particular application. For example, use of a non-hazardous chemical (e.g., nitrates) may be prudent for one application; whereas, the use of a fast reacting chemical (e.g., hypochlorite) may be needed for another. Generally, however, economics is the dominant selection criterion. In that regard, there are two chemicals (excluding gas chlorine) that provide the lowest theoretical costs: iron salts and hydrogen peroxide (if used in the oxidation mode).

**Figure 3. Comparative costs for alternative sulfide control chemical treatments**

Chemical Reactant	Chemical Cost		Theoretical Weight Ratio (lbs/ lb-H <sub>2</sub> S)
	(Basis)	(\$/lb-100%)	
Chlorine (gas)	\$ 150/ton	0.075	9.0
Sodium hypochlorite	\$0.50/gal-15%	0.309	9.0
Ferric chloride	\$0.070/lb-40%	0.175	3.2
Ferrous chloride	\$0.045/lb-25%	0.180	3.7
Hydrogen peroxide (Oxidation)	\$0.345/lb-50%	0.690	1.0
(Prevention)	\$0.345/lb-50%	0.690	4.0
Potassium permanganate	\$1.45/lb-98%	1.378	3.1
Calcium/sodium nitrate (NO <sub>3</sub> )	\$0.35/lb-NO <sub>3</sub>	0.350	3.2
Sodium chlorite	\$0.40/lb-25%	1.600	1.4

*Iron salts* are perhaps the most widely used sulfide control agent in the municipal wastewater industry, and find particular utility for applications within collection systems and solids processing operations. The ferrous products control sulfide by converting (volatile) dissolved sulfide into (non-volatile) ferrous sulfide, which appears as a black precipitate.

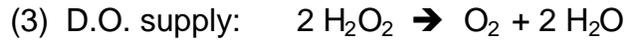
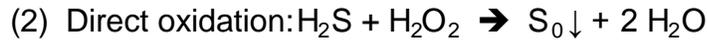


The theoretical chemical requirement is 1.7 lbs Fe (or 3.7 lbs FeCl<sub>2</sub>) per lb-Sulfide. In addition to low cost, iron salts afford control of H<sub>2</sub>S for several hours and are less impacted by the oxygen demand of the wastewater. To the extent that residual free iron (not FeS) is present at the plant headworks, primary clarification and digester H<sub>2</sub>S control can be improved. However, as discussed later, the use of iron salts may pose problems related to solids production, alkalinity, and salinity.

**Figure 4. Advantages and disadvantages of using iron salts for collection system sulfide control**

<b>Iron Salts (alone)</b>	
<u>Advantages</u>	<u>Disadvantages</u>
Affords long-duration control	Adverse by-products (solids, salinity, acidity)
Not impacted by O <sub>2</sub> uptake rates	Diminishing returns at low sulfide levels
Provides plant benefits (clarification, digesters)	Depletion of dissolved oxygen

*Hydrogen peroxide* (H<sub>2</sub>O<sub>2</sub>) is also widely used within the municipal wastewater industry, though its utility is primarily for headworks treatment (to oxidize sulfide in the influent sewers) and less so for collection systems. H<sub>2</sub>O<sub>2</sub> controls sulfide by one of two mechanisms: direct oxidation of sulfide to elemental sulfur; and prevention of sulfide formation by supply of dissolved oxygen to the wastewater.



Where H<sub>2</sub>O<sub>2</sub> is added to remove sulfide already present, the first reaction applies and the theoretical chemical requirement is 1.0 lbs H<sub>2</sub>O<sub>2</sub> per lb-Sulfide. Where H<sub>2</sub>O<sub>2</sub> is added to prevent the downstream generation of sulfide, the second reaction applies and the theoretical chemical requirement is 4.0 lbs H<sub>2</sub>O<sub>2</sub> per lb-Sulfide. These two distinct modes of application (direct oxidation versus D.O. supply) are the most likely explanation for the wide variation in values reported in the literature.

When used in its low cost (direct oxidation) mode, H<sub>2</sub>O<sub>2</sub> oxygenates the wastewater and produces fewer solids (1 lb per lb-Sulfide controlled, regardless of H<sub>2</sub>O<sub>2</sub> dose). However, when used in the prevention mode (to control downstream generation), H<sub>2</sub>O<sub>2</sub> is considerably more costly and is adversely impacted by factors such as retention time and O<sub>2</sub> uptake. For example, practical requirements in the prevention (D.O. supply) mode can be 2-4x theoretical when retention times increase > 3-4 hours. For these reasons, most H<sub>2</sub>O<sub>2</sub> applications within the municipal wastewater industry are for headworks odor control, where the H<sub>2</sub>O<sub>2</sub> can be applied in its most efficient manner – as an oxidant.

**Figure 5. Advantages and disadvantages of using H<sub>2</sub>O<sub>2</sub> for collection system sulfide control**

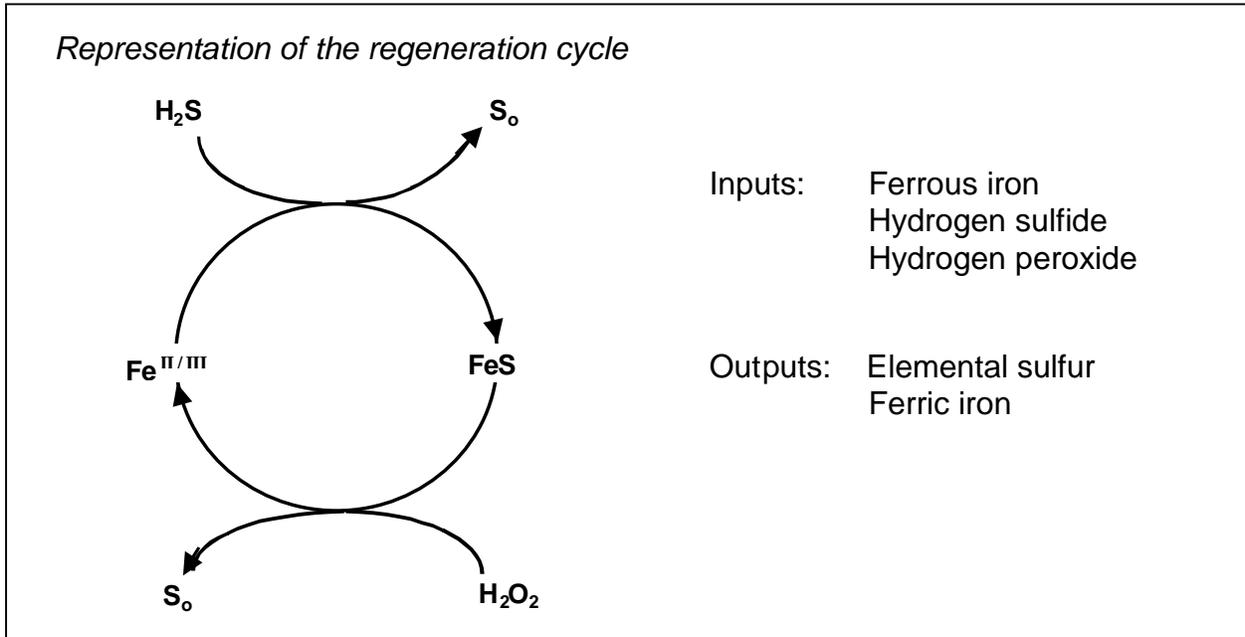
<b>H<sub>2</sub>O<sub>2</sub> (alone)</b>	
<u>Advantages</u>	<u>Disadvantages</u>
Adds no adverse by-products Oxygenates the wastewater	Control for > 1-2 hours is costly Adversely affected by high O <sub>2</sub> uptake rates

**The PRI-SC technology**

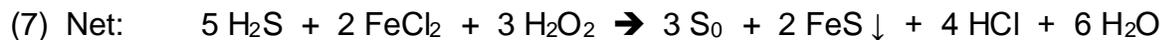
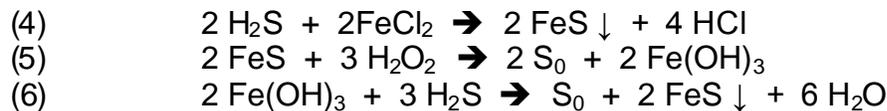
The PRI-SC technology involves using iron salts as the primary sulfide control agent, and using H<sub>2</sub>O<sub>2</sub> to regenerate the “spent” iron (predominantly FeS) at one or more points downstream. The analogy is one of a capturing agent (iron salt) added at the top of an interceptor, which then adsorbs dissolved sulfide as it moves down the line. Intermittent H<sub>2</sub>O<sub>2</sub> injection serves to regenerate the capturing agent thereby allowing additional sulfide to be absorbed downstream. At the final regeneration point (the

treatment plant), the resultant hydrous ferric oxide oxidation product is available to enhance primary clarification. The combination treatment may thus be viewed as a regeneration cycle, with an oxidant ( $H_2O_2$ ) oxidizing the spent iron salt ( $FeS$ ) *in-situ* – yielding ferrous / ferric iron and colloidal sulfur.

**Figure 6. Peroxide Regenerated Iron – Sulfide Control (PRI-SC)<sup>tm</sup>**



The reaction steps in one regeneration cycle are thus: 1) iron complexation with dissolved sulfide (similar to use of ferrous iron alone); 2)  $H_2O_2$  oxidation of the  $FeS$  complex to provide elemental sulfur and free iron (hydrous ferric oxide); and 3) oxidation and complexation of additional sulfide by the ferric iron to produce elemental sulfur and  $FeS$ . The net reaction requires 0.7 lbs Fe (or 1.5 lbs  $FeCl_2$ ) and 0.6 lbs  $H_2O_2$  per lb-Sulfide. This yields a theoretical control cost of about \$0.68 per lb-Sulfide, per the unit prices listed in Figure 3.

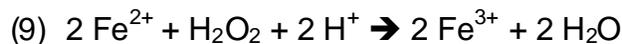
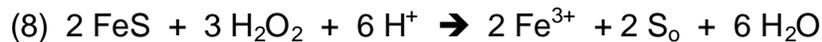


In addition to the benefits afforded by iron salts and  $H_2O_2$  (used independently), the combination as employed in PRI-SC affords some important benefits not easily available from either chemical used by alone. For example, practical control of sulfides to very low levels (e.g., < 0.1 mg/L) is afforded by PRI-SC with minimal reaction time (within 1-2 minutes). Further, PRI-SC eliminates or greatly reduces the negative water quality impacts associated with using iron salts alone (discussed later).

**Figure 7. Advantages and disadvantages of using PRI-SC for collection system sulfide control**

<b>Iron – Peroxide (combination)</b>	
<u>Advantages</u>	<u>Disadvantages</u>
Affords long-duration control Not impacted by oxygen demand Provides plant benefits (clarification, digesters) Oxygenates the wastewater Practical control to low sulfide levels Rapid oxidation reaction	Small impact on solids, alkalinity & salinity

At the final regeneration point (the treatment plant), the oxidation by H<sub>2</sub>O<sub>2</sub> of combined sulfide (FeS) and residual ferrous iron becomes important as regards enhanced primary clarification. Significantly, the economics for performing equation (8) are favorable when compared the cost for adding FeCl<sub>3</sub> (as discussed later). The use of equation (9) for enhanced clarification has been described for the ferrous coagulation of humic substances in terms of reducing THMFP in drinking waters (Kang and Yen, 1995).



### **Study objectives**

The objectives of four month initial study were three-fold:

1. To prove the concept underlying the PRI-SC technology – i.e., using H<sub>2</sub>O<sub>2</sub> to convert spent FeS to free iron available for subsequent sulfide control and/or enhanced clarification;
2. To profile the dose-response efficiency of FeCl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> feed rates to control liquid and vapor sulfide levels within the collection system, targeting treatment levels of 0.5 mg/L dissolved sulfide and 25 ppm vapor H<sub>2</sub>S; and
3. To characterize the impact of the PRI-SC program on treatment plant operations, particularly the FeCl<sub>3</sub> feed rates needed to affect advanced primary treatment.

## **METHODOLOGY**

### **Interceptor characteristics**

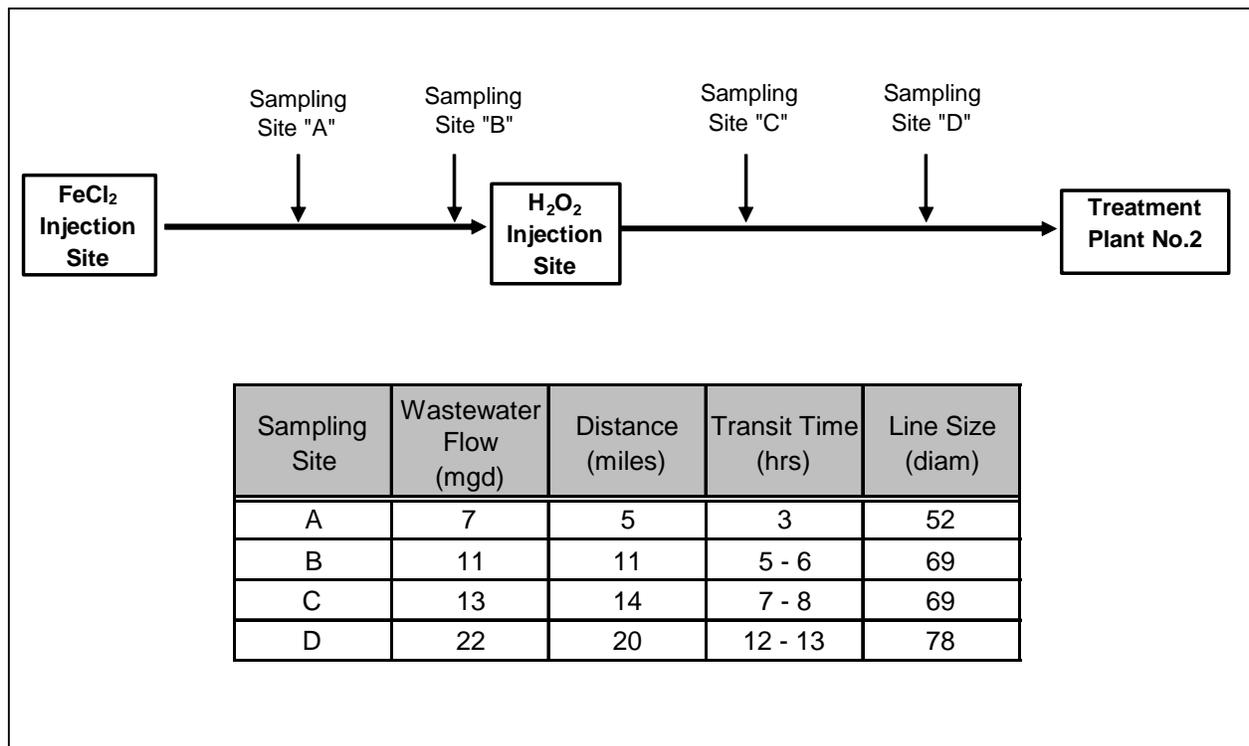
The study involved three major interceptors (the Miller-Holder, the Knott-Interplant, and the Baker-Main) with characteristics described in Figure 8.

**Figure 8. Characteristics of the interceptors studied**

Interceptor	Flow (MGD) into WWTP	Distance (miles)	Transit Time (hrs) from FeCl <sub>2</sub>	Total (Aqueous) Sulfide	
				Conc. (mg/L)	Loading (lbs/day)
<b>Miller - Holder</b>	<b>23</b>	<b>25</b>	<b>14</b>	<b>10</b>	<b>1,919</b>
Knott - Interplant	80	17	13	3	1,869
Baker - Main	15	9	7	9	1,064

For brevity, only the Miller-Holder information is discussed in this paper. The Miller-Holder interceptor is generally described as a long, slow flowing, high sulfide-producing sewer. Except for contributing force main discharges just prior to the midway point, and a siphon just after the midway point, the interceptor is a free-flowing gravity RCP with average velocity 2.1 fps and diameters increasing from 48" (at the FeCl<sub>2</sub> injection point) to 78" (at the treatment plant). The wastewater is typical of mixed residential – commercial origins, with no major industrial inputs. Figure 9 shows the location of chemical injection and sampling points. FeCl<sub>2</sub> was injected at the top of the interceptor where flows were approx. 5 MGD, and H<sub>2</sub>O<sub>2</sub> was injected first at the midway point where flows were approx. 16 MGD and again at the treatment plant into the influent sewer.

**Figure 9. Schematic of the Miller – Holder Interceptor system**



## Chemical storage / feed

Each chemical installation used in the study consisted of a double-walled HDPE storage tank, a pump module, and secondary containment system. The pump module included a computer-controlled output with the hourly feed rates profiled to match sulfide loadings, and a cellular telemetry system to monitor pump performance, adjust feed rate profiles, and manage chemical inventories (tank levels).

The iron was supplied as a 35-36% w/w  $\text{FeCl}_2$  solution (1.9 lbs-Fe per gallon); whereas the  $\text{H}_2\text{O}_2$  was supplied as a 50% w/w solution (5.0 lbs- $\text{H}_2\text{O}_2$  per gallon).

**Figure 10.  $\text{FeCl}_2$  and  $\text{H}_2\text{O}_2$  installations**



**Figure 11. Chemical pump module**



## Analytical methods

Continuous vapor  $\text{H}_2\text{S}$  monitoring / datalogging was performed throughout the study at the five sites along the interceptor identified in Figure 8. Liquid determinations were by periodic grab sampling except for diurnal profiles which were by sequential autosamplers.

**Figure 12. Analytical methods used in the field tests**

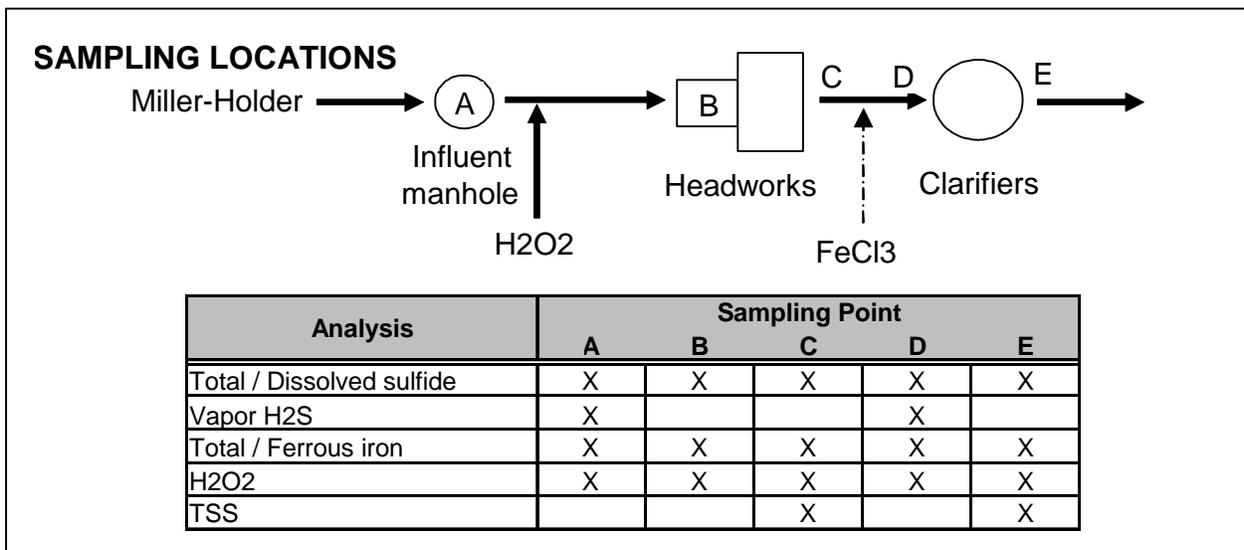
Sample Type	Procedure
<u>Liquid (grab) samples</u>	
Total sulfide	Std. Methods 4500-S <sup>2-</sup> D. Methylene Blue (Lamotte drop count)
Dissolved sulfide	Ditto, using pre-flocculation to remove insoluble sulfides
pH	Combination glass electrode
Temperature	NIST calibrated thermometer
Total iron	Std. Methods 3500-Fe D. Phenanthroline (Hach colorimeter)
Ferrous iron	Ditto, without reductive pretreatment
Ferric iron	Calculated by difference (total iron – ferrous iron)
Residual H <sub>2</sub> O <sub>2</sub>	Enzymatic redox test strips (e.g., EM Quant)
<u>Vapor samples (continuous datalogging)</u>	
H <sub>2</sub> S	App-Tek Odalog (monitor / datalogger)

**Chemical dosages**

Initial feed rates in the collection system (960 gpd FeCl<sub>2</sub>-36% and 300 gpd H<sub>2</sub>O<sub>2</sub>-50%) were based on the theoretical amounts needed to control the mass of sulfide determined in the baseline survey – i.e., 1900 lbs-Sulfide per day. The daily feed rates were held constant and each chemical was alternately dosed more or less to develop a response profile. Hourly feed rates were paced by computer to historical vapor H<sub>2</sub>S levels, and tuning of the feed rate profile proceeded over several weeks to equalize the diurnal peaks and valleys in the downstream H<sub>2</sub>S profile.

For the study on treatment plant credits, H<sub>2</sub>O<sub>2</sub> feed rates to the influent sewer were incrementally increased (typically at weekly intervals) while FeCl<sub>3</sub> feed rates to the clarifiers were incrementally lowered (typically at 2-3 day intervals). Total Suspended Solids (TSS) levels were determined hourly in overflow samples from the selected clarifier, while other analyses were performed on periodic grab samples throughout the day (Figure 13).

**Figure 13. Sampling program for treatment plant**



## RESULTS

### Proof of Concept

The concept underlying the PRI-SC technology (i.e., regeneration by H<sub>2</sub>O<sub>2</sub> of spent FeS to ferrous/ferric iron) was evidenced by the following upon H<sub>2</sub>O<sub>2</sub> addition:

1) *Removal of Total Sulfide (predominantly FeS).* Total sulfide levels prior to the midpoint H<sub>2</sub>O<sub>2</sub> injection site were typically 10 mg/L while those 30-45 minutes downstream of the H<sub>2</sub>O<sub>2</sub> injection site were < 0.2 mg/L.

2) *Conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup>.* Ferrous iron levels prior to the treatment plant H<sub>2</sub>O<sub>2</sub> injection site were typically 8-9 mg/L while those 5-10 minutes downstream at the headworks were < 1 mg/L, indicating a conversion of 85-90%.

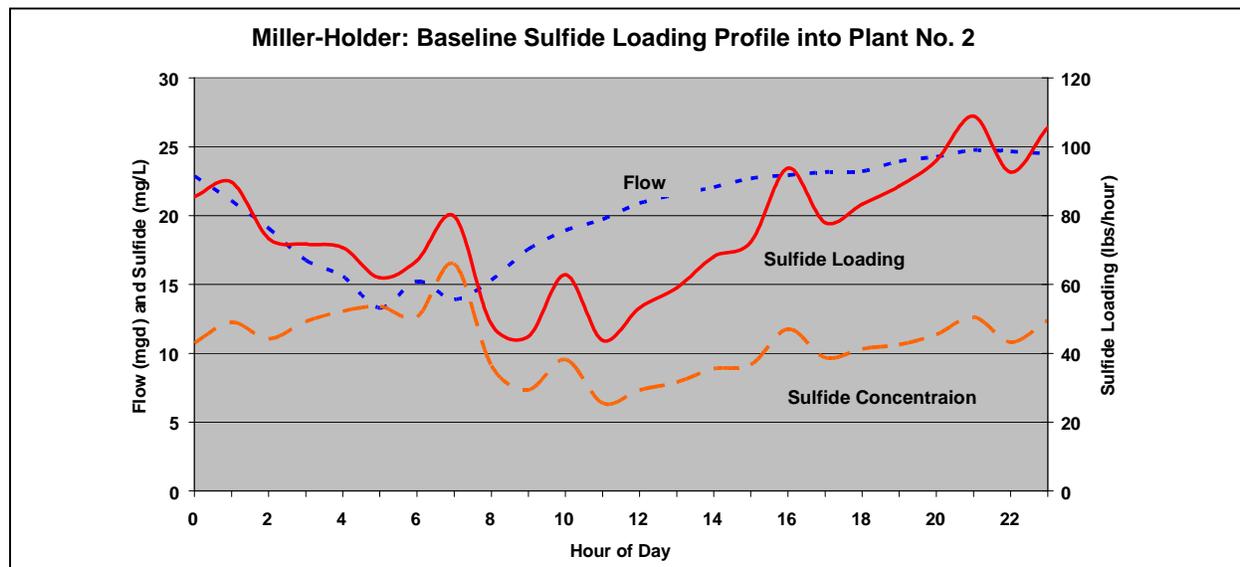
3) *Efficiency of sulfide removal.* The input of 2000 lbs per day of iron in the upper reaches of the interceptor was, with H<sub>2</sub>O<sub>2</sub> injection at the midpoint, able to control 1900 lbs per day of dissolved sulfide. This translates to an efficiency of 1.0 lb iron per lb sulfide, which is 57% of the amount theoretically needed were H<sub>2</sub>O<sub>2</sub> not added at the midpoint.

4) *Reduction in FeCl<sub>3</sub> requirements (for enhanced primary clarification).* As shown later in the paper, FeCl<sub>3</sub> feed rates at the treatment plant were reduced by almost stoichiometric amounts to the FeCl<sub>2</sub> feed rates upstream in the interceptor, with no apparent loss in clarification effectiveness.

### Collection system study

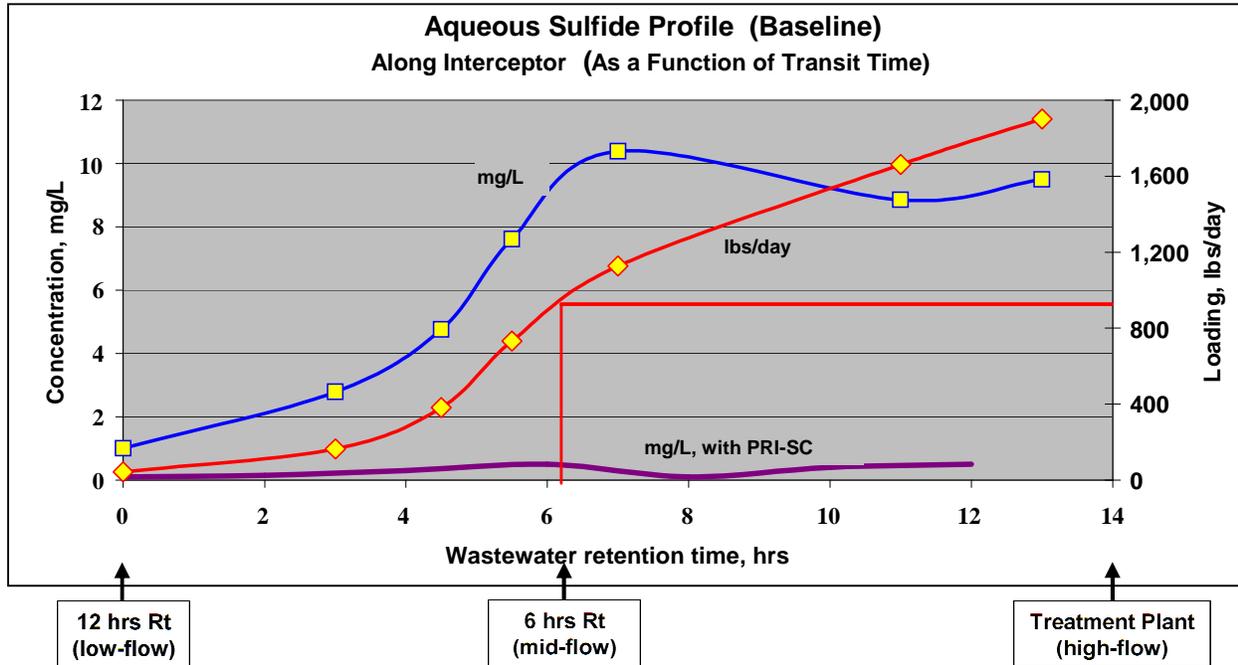
With no chemical treatment, the sulfide mass loading profile at the interceptor terminus (into the treatment plant) is shown in Figure 14. The graph indicates a daily loading of approx. 1900 lbs of total sulfide, with the lower levels occurring in the late morning and the higher levels occurring in the late evening.

**Figure 14. Diurnal sulfide variation at treatment plant influent**



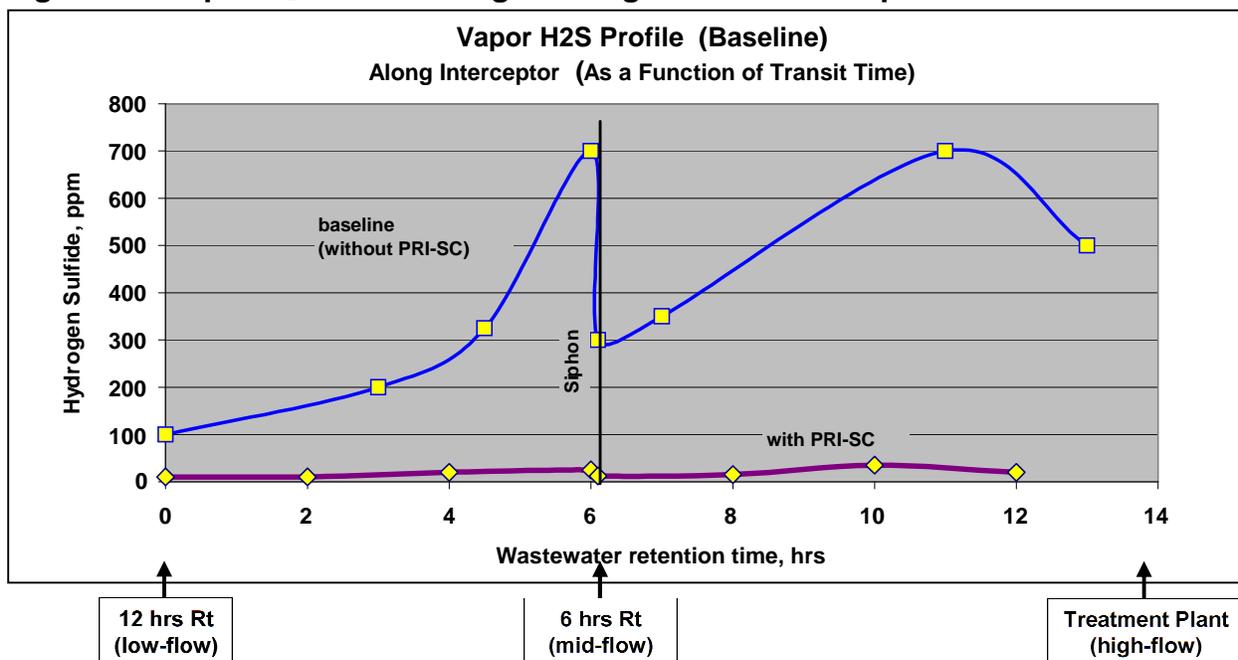
The sulfide mass loadings along the interceptor are shown in Figure 15 (below). The levels peak at 10-12 mg/L just over halfway down the interceptor, after which inputs of fresh wastewater dilute the levels to 8-10 mg/L by treatment plant.

**Figure 15. Aqueous sulfide generation along the length of the interceptor**



The vapor H<sub>2</sub>S levels likewise increased along the interceptor, with values ranging from 250 ppm to 1000 ppm. Figure 16 (below) shows the typical diurnal profile of vapor H<sub>2</sub>S levels. The effect of the siphon on these levels is notable even though air jumpers are in place to minimize the restriction.

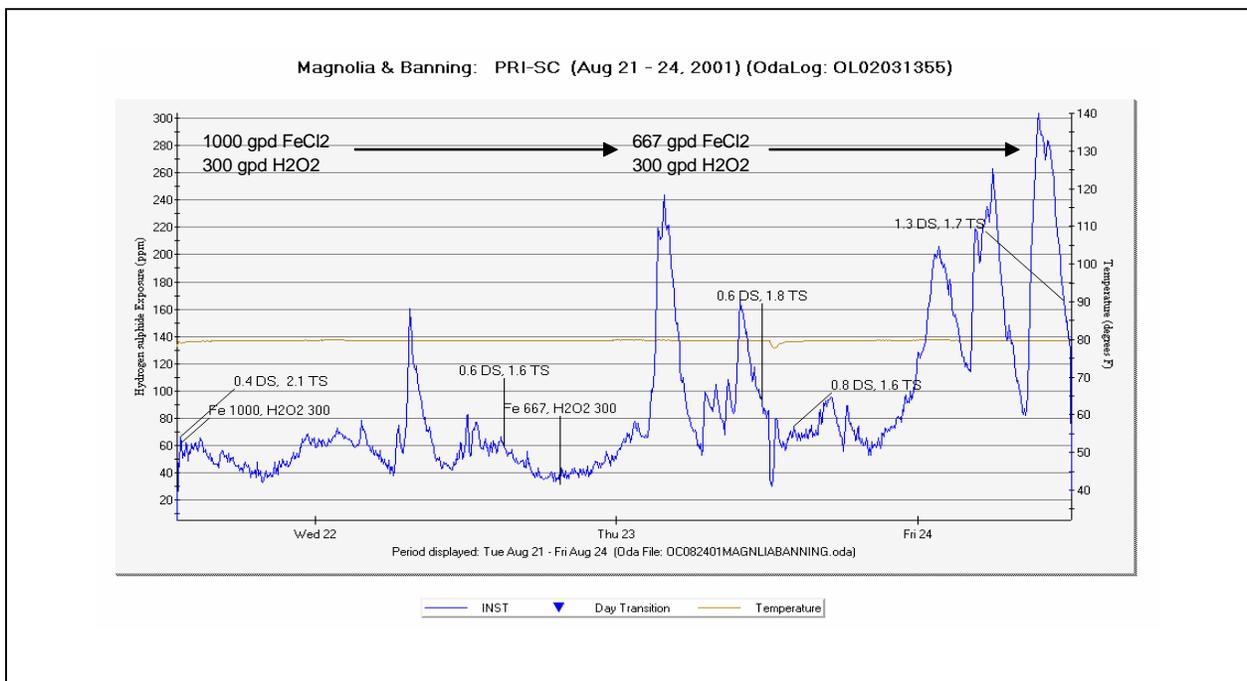
**Figure 16. Vapor H<sub>2</sub>S levels along the length of the interceptor**



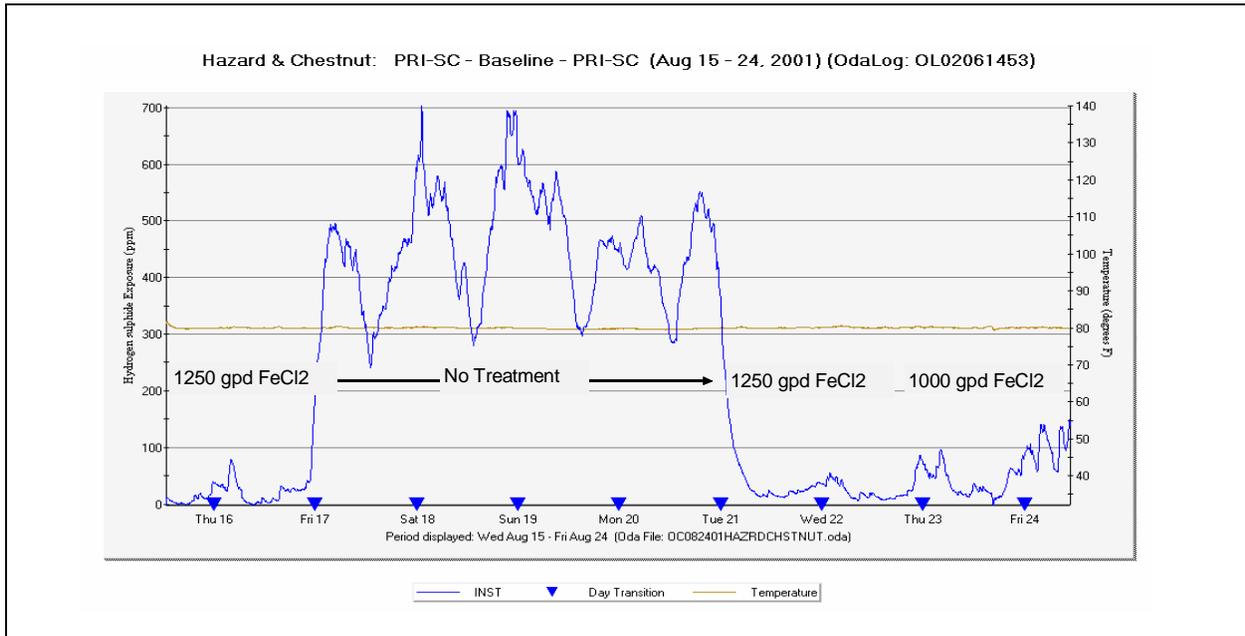
With regard to optimizing the PRI-SC feed rates, four FeCl<sub>2</sub> feed rates were tested: 667 gpd, 1000 gpd, 1250 gpd and 1500 gpd while the midpoint H<sub>2</sub>O<sub>2</sub> feed rates were held constant. Figure 17 (below) shows vapor H<sub>2</sub>S levels of 40-70 ppm for the 1000 gpd feed rate (90% reduction) and 100-250 ppm for the 667 gpd rate (80% reduction). Vapor H<sub>2</sub>S levels at the 1250 gpd rate (not shown) were typically 25-50 ppm (95% reduction). Significantly, the 1500 gpd rate did not produce a discernible improvement over 1250 gpd.

Figure 18 shows the vapor H<sub>2</sub>S levels prior to the midpoint H<sub>2</sub>O<sub>2</sub> injection site when 1000 gpd and 1250 gpd FeCl<sub>2</sub> were added. The former produced levels of 50-125 ppm (80% removal) whereas the latter produced levels of 20-40 ppm (95% removal). Corresponding liquid sulfide levels averaged 0.5 mg/L dissolved sulfide and 3.6 mg/L total sulfide for the 1000 gpd rate, and 0.4 mg/L and 2.8 mg/L, respectively, for the 1250 gpd rate.

**Figure 17. Sample vapor H<sub>2</sub>S profile (near the interceptor terminus) showing the effect of FeCl<sub>2</sub> feed rates**



**Figure 18. Sample vapor H<sub>2</sub>S profile (near the midpoint prior to H<sub>2</sub>O<sub>2</sub> injection) showing the effect of FeCl<sub>2</sub> feed rates**



Three H<sub>2</sub>O<sub>2</sub> feed rates at the midpoint site were studied: 225 gpd, 300 gpd and 375 gpd – holding the upstream FeCl<sub>2</sub> feed rate constant at 1000 gpd. A rate of 225 gpd lowered the H<sub>2</sub>S levels near the interceptor terminus to 100-200 ppm (80% removal), whereas a rate of 300 gpd lowered the levels to 40-60 ppm (95% removal). The corresponding liquid levels were 0.8 and 0.4 mg/L for the 225 gpd and 300 gpd rate, respectively. No discernible improvement was observed when the rate was increased to 350 gpd.

The H<sub>2</sub>O<sub>2</sub> requirement at the treatment plant (to trim incoming dissolved sulfide levels to < 0.5 mg/L) was not determined, but industry experience would predict the demand to be around 50 gpd.

The optimal daily feed rates were determined to be 1000 - 1250 gpd FeCl<sub>2</sub> and 300 – 325 gpd H<sub>2</sub>O<sub>2</sub> (at the midpoint site). At these rates, dissolved sulfide levels were maintained at 0.1 - 0.5 mg/L at most points along the interceptor except near the terminus where local saltwater infiltration may be an issue (values of 0.6 - 0.8 mg/L were typical). This represents a 90-95% reduction in the sulfide mass. These feed rates controlled vapor H<sub>2</sub>S levels to < 25 ppm (35-40 ppm near the terminus).

### Treatment plant results

Regarding odor impacts at the treatment plant, with the existing program (periodic caustic shocking with H<sub>2</sub>O<sub>2</sub> added to the influent sewer), dissolved sulfide levels in the influent ranged from 0.5 – 10 mg/L, and vapor H<sub>2</sub>S levels to the influent sewer scrubbers were typically from 50 – 500 ppm, depending on the time passed since the last caustic shock. Adding 450 gpd H<sub>2</sub>O<sub>2</sub> to the influent sewer removed 75 – 90% of the

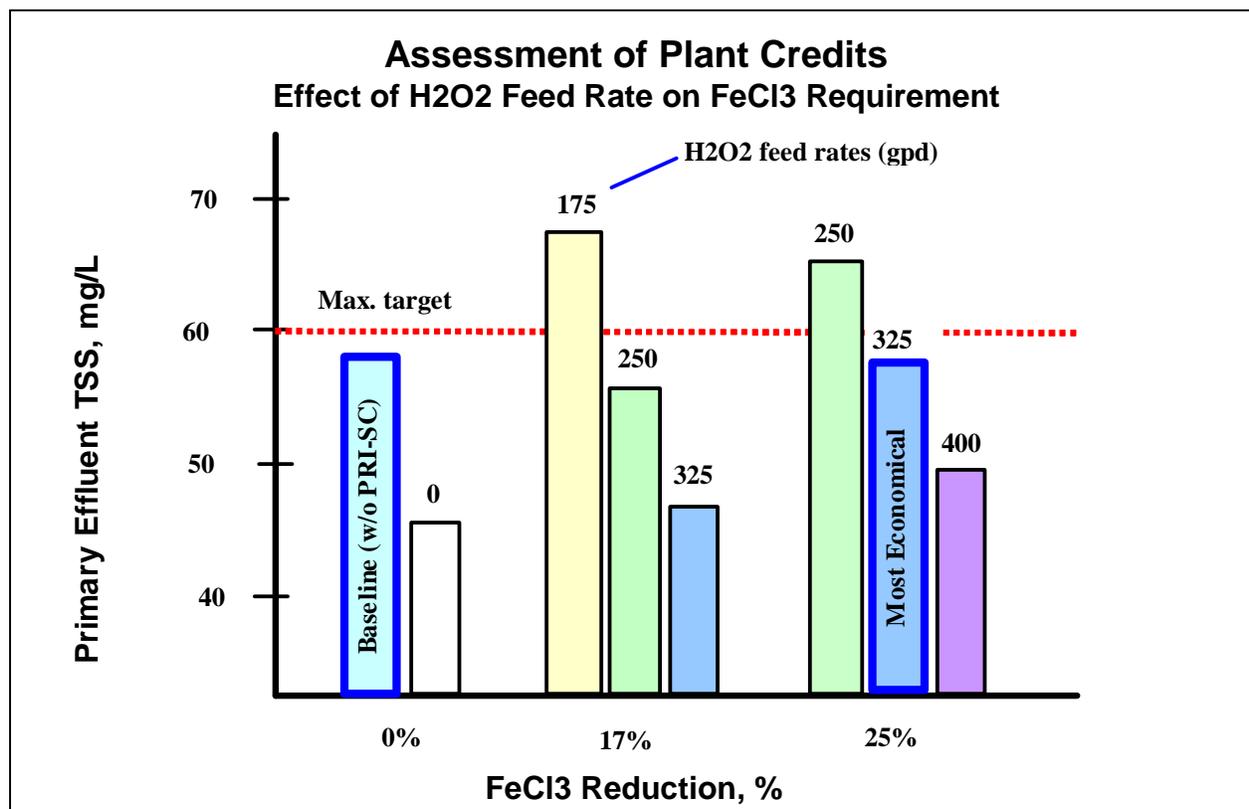
sulfide from the wastewater within the 5 – 10 minute transit time to the headworks facility, though a 2–3:1 dose rate was needed to drive the reaction.

Dosing at the optimized PRI-SC rates within the collection system provided control of dissolved sulfide to < 0.5 mg/L into the treatment plant. Vapor H<sub>2</sub>S levels to the influent sewer scrubbers were reduced to about 10 ppm – this was achieved without any H<sub>2</sub>O<sub>2</sub> added to the influent sewers. With 325 gpd H<sub>2</sub>O<sub>2</sub> added to the influent sewer to oxidize FeS and regenerate ferrous iron, the dissolved sulfide levels were reduced to < 0.1 mg/L within the 5 – 10 minute transit time. This level treatment had a notable positive impact on the odors around the plant generally ascribed to fugitive emissions.

Regarding the primary clarification impacts at the treatment plant, TSS values in the primary clarifier effluent historically averaged 56 mg/L, with a typical range of 50 – 70 mg/L (the target range is 45 – 60 mg/L). To achieve these results, the plant adds approx. 4300 gpd FeCl<sub>3</sub>-42% (dose: 6 mg/L Fe) and 37 lbs per day of anionic polymer (dose: 0.3 mg/L).

Figure 19 (below) shows that the amount of FeCl<sub>3</sub> needed to maintain a value of < 60 mg/L TSS decreased as the H<sub>2</sub>O<sub>2</sub> feed rate into the influent sewer increased. With no H<sub>2</sub>O<sub>2</sub> added to the influent sewer and no reduction in FeCl<sub>3</sub> feed rates, the TSS values were reduced to 45 mg/L. The improvement is most likely due to the high levels of residual free iron present in the influents receiving upstream PRI-SC treatment, combined with partial Fe<sup>2+</sup> oxidation through the aerated grit basins and/or by residual H<sub>2</sub>O<sub>2</sub> present in the other (commingled) influents.

**Figure 19. Plant credits for FeCl<sub>3</sub> (enhanced primary clarification)**



Four of the six H<sub>2</sub>O<sub>2</sub> / FeCl<sub>3</sub> feed rate combinations tested produced TSS values that met the < 60 mg/L target value. Considering the unit costs for H<sub>2</sub>O<sub>2</sub> and FeCl<sub>3</sub>, the most economical feed rate scenario was 325 gpd H<sub>2</sub>O<sub>2</sub> into the influent sewer and a 25% reduction in FeCl<sub>3</sub> use which equates to 1000 gpd FeCl<sub>3</sub>.

## **DISCUSSION**

### **Collection system results**

Given the baseline sulfide loading of 1900 lbs per day sulfide, the stoichiometric requirements for FeCl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> for the Miller-Holder interceptor are approx. 950 gpd and 250 gpd, respectively. This indicates the actual efficiencies achieved in the field (1000 gpd and 300 gpd) were within 20% of theory.

The most important factor in optimizing PRI-SC efficiency occurs when selecting the location of the H<sub>2</sub>O<sub>2</sub> sites. Optimal deployment of PRI-SC specifies that the H<sub>2</sub>O<sub>2</sub> sites be located at equally spaced intervals in terms of sulfide mass loading. For example, with two regeneration sites within the collection system, the H<sub>2</sub>O<sub>2</sub> sites would ideally be spaced at the points by which 33% and 67% of the sulfide mass passes. In this instance, where one regeneration site was used, the midway H<sub>2</sub>O<sub>2</sub> site was situated at the point along the interceptor where the sulfide loading is 50% of that where the interceptor terminates into the treatment plant (i.e., the point where the sulfide loading was 950 lbs per day). Since site available is almost always an issue, practical limitations often preclude such optimal deployment, though that was fortunately not case in this study.

While the target sulfide control levels were achieved for most of the 25 mile length of the interceptor, there were local areas that proved difficult to control. There are many possible explanations for this – turbulence, lateral vapor inputs, restricted vapor flows, saltwater infiltration, etc. These are currently the subject of investigation for future studies.

### **Treatment plant credits**

As stated earlier, dosing at the optimized PRI-SC rates within the collection system provided control of dissolved sulfide to < 0.5 mg/L into the treatment plant. This was achieved without any H<sub>2</sub>O<sub>2</sub> added to the influent sewers, which represented a credit of 450 gpd, which is equal to about 40% of the upstream PRI-SC costs. However, 85-90% of the iron present in the influent flow was ferrous iron, which OCSD had previously determined to be about 50% less efficient than Fe<sup>3+</sup> in enhancing clarification. Therefore, a key component of the PRI-SC technology is to add H<sub>2</sub>O<sub>2</sub> a final time to the influent sewers in order to oxidize FeS and ferrous iron to ferric iron.

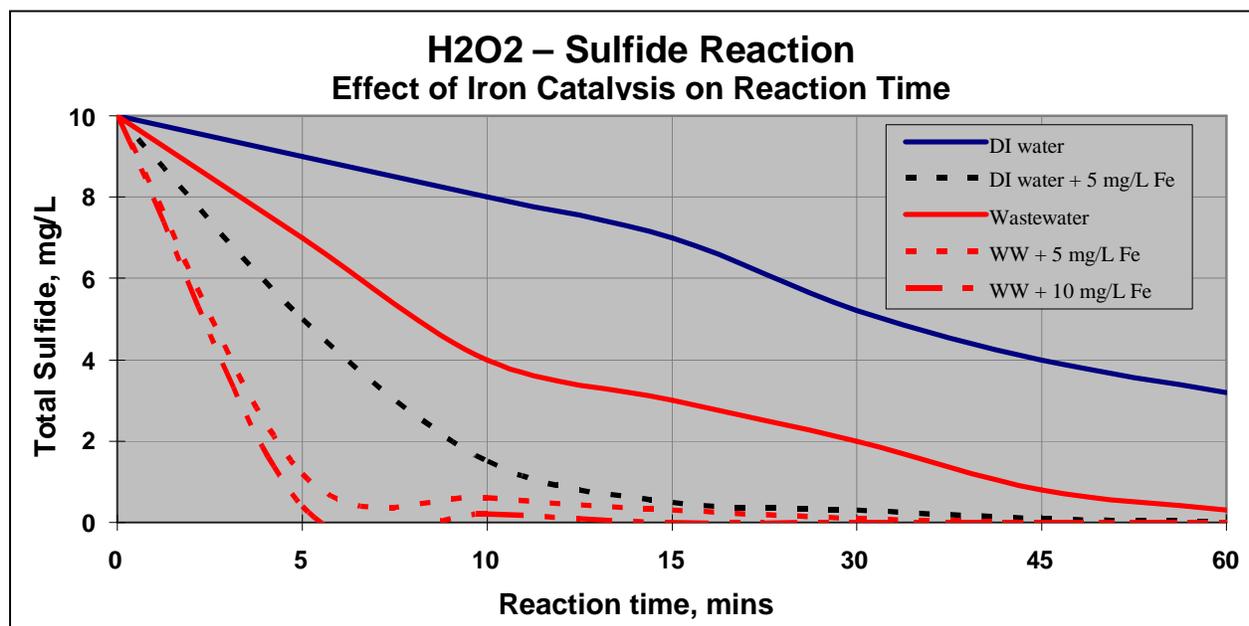
Since 36% FeCl<sub>2</sub> contains 1.9 lbs-Fe per gallon and 42% FeCl<sub>3</sub> contains 1.7 lbs-Fe per gallon, one gallon of 36% FeCl<sub>2</sub> added in the collection system, if oxidized as it enters the treatment plant, could theoretically replace 1.1 gallons of 42% FeCl<sub>3</sub>. Significantly, the typical price differential between the two iron products suggests oxidation of the Fe<sup>2+</sup> with H<sub>2</sub>O<sub>2</sub> at the treatment plant to be 20-30% more efficient than adding Fe<sup>3+</sup> (as

FeCl<sub>3</sub>). Ferrous and ferric iron levels measured before and after H<sub>2</sub>O<sub>2</sub> injection at the treatment plant showed Fe<sup>2+</sup> conversions of 85-90% within 5-10 minutes, on H<sub>2</sub>O<sub>2</sub> utilization efficiencies of about 85%. Given the 1000 gpd upstream FeCl<sub>2</sub> feed into the Miller-Holder interceptor, the expected FeCl<sub>3</sub> credit at the plant was thus about 1000 gpd, or about 23% of the historical requirement. This value was confirmed in the clarifier TSS study whereby no discernible increase in effluent TSS levels was observed upon reducing the FeCl<sub>3</sub> feed by 25%. This feature of the PRI-SC technology predicts that it may be warranted to increase the FeCl<sub>2</sub> feed in the collection system in place of FeCl<sub>3</sub> feed at the treatment plant, thereby affording further reductions in sulfide levels within the collection system.

Other benefits accrued by adding H<sub>2</sub>O<sub>2</sub> to the Plant-2 influents, such as reduced H<sub>2</sub>S loadings to the influent scrubbers (> 95% reduction in H<sub>2</sub>S levels in the influent sewers). Though savings in the headworks scrubbers were not quantified in this initial study, they should also be significant since the addition of H<sub>2</sub>O<sub>2</sub> quickly drives the dissolved sulfide levels from 0.5 mg/L to < 0.1 mg/L. Further, constraints of limited reaction time – a problem inherent at the OCS D treatment plant – were eliminated through the combination of low influent sulfide levels and high iron values (a catalyst for accelerating the H<sub>2</sub>O<sub>2</sub> – Sulfide reaction).

The catalytic effect of transition metals on rate of sulfide oxidation is well-known. Figure 20 (below) graphs the results of a laboratory study that shows this effect. In the case of the Miller-Holder, the presence of 8-10 mg/L Fe in the plant influent reduced the required reaction time from e.g., 20-30 minutes to < 5 minutes. The catalysis also economizes H<sub>2</sub>O<sub>2</sub> use – not only is overfeeding H<sub>2</sub>O<sub>2</sub> to drive sulfide oxidation not needed but, by accelerating to reaction to < 5 minutes, there is less opportunity for the H<sub>2</sub>O<sub>2</sub> to decay into dissolved oxygen (which is the primary side reaction in using H<sub>2</sub>O<sub>2</sub> to oxidize sulfide).

**Figure 20. Effect of iron catalysis on the required H<sub>2</sub>O<sub>2</sub> – Sulfide reaction time**



Reaction conditions: pH 7.6, 22 deg-C, dose ratio of H<sub>2</sub>O<sub>2</sub> : S = 1.5, Fe added as FeCl<sub>2</sub>

## Net costs

Figure 21 (below) presents the cost breakdown for the PRI-SC technology. The resulting cost to control to < 0.5 mg/L dissolved sulfide for the length of the 25 mile interceptor was \$1.02 per lb-Sulfide (excluding plant credits). However, this cost must be offset by realizing at the treatment plant either an H<sub>2</sub>O<sub>2</sub> credit (since H<sub>2</sub>O<sub>2</sub> added to the influent sewer was no longer needed to remove dissolved sulfide) or a FeCl<sub>3</sub> credit (since continued H<sub>2</sub>O<sub>2</sub> addition to the influent sewer would result in Fe<sup>2+</sup> conversion to Fe<sup>3+</sup>). Were one to take the H<sub>2</sub>O<sub>2</sub> credit (450 gpd, or \$720 per day) the adjusted (net) program costs would be \$0.64 per lb-Sulfide; whereas, were one to take the FeCl<sub>3</sub> credit (1000 gpd, or \$990 per day including the partial H<sub>2</sub>O<sub>2</sub> credit), the adjusted (net) program costs would be \$0.49 per lb-Sulfide.

Significantly, this cost reflects the entire program cost which includes chemical supply, chemical storage / dosing equipment, and application monitoring / reporting. Other likely credits associated with reduced vapor H<sub>2</sub>S loadings to the odor scrubbers are not included.

**Figure 21. Optimal net cost for utilizing the PRI-SC program (Miller-Holder Interceptor)**

PRI-SC Program	Feed Rate gpd	Projected Annual Costs
<b>Collection system</b>		
Ferrous chloride - 36%	1,000	\$1,180
Hydrogen peroxide - 50%	300	\$750
		-----
<b>Subtotal costs</b>		<b>\$1,930</b>
<b>\$ per lb-S</b>		<b>\$1.02</b>
<b>Plant credits available</b>		
Hydrogen peroxide - 50% (saved)	125	(\$200)
Ferric chloride - 42% (saved)	1,000	(\$790)
		-----
<b>Subtotal credits</b>		<b>(\$990)</b>
<b>Net Cost</b>		<b>\$940</b>
<b>\$ per day</b>		
<b>\$ per lb-S</b>		<b>\$0.49</b>

**NOTES:**

- 1) PRI-SC program costs (includes associated equipment and services) = \$1.18/gal (FeCl<sub>2</sub>-36%, \$2.50/gal (H<sub>2</sub>O<sub>2</sub>-50%))
- 2) Treatment plant unit chemical costs = \$0.79/gal (FeCl<sub>3</sub>-42%) or \$310 per dry ton, and \$1.60/gal (H<sub>2</sub>O<sub>2</sub>-50%)

## PRI-SC chemistry

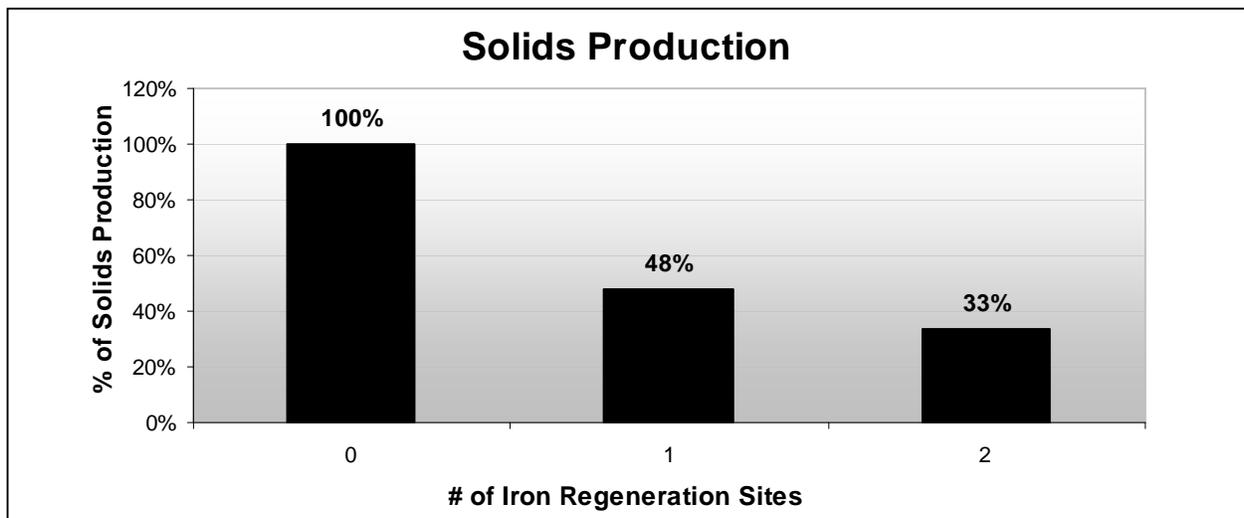
Combination treatments have been examined by several studies to improve the cost-effectiveness of iron salts and/or  $H_2O_2$  for sulfide (odor) control. The use of  $H_2O_2$  to oxidize  $Fe^{2+}$  is well-established and is frequently used to remove iron from groundwaters and acid mine drainage.  $H_2O_2$  has also been used in certain processes for producing commercial ferric sulfate (personal communication, 1992). One particular version of the  $Fe^{2+}$  and  $H_2O_2$  combination (termed “Fenton’s Reagent”) was first reported over a hundred years ago (Fenton, 1894), and is widely employed today for destroying recalcitrant and/or toxic organics present in industrial wastes or contaminating soils and groundwaters (Watts, 1990). However, as will be discussed later, the PRI-SC technology is not believed to involve Fenton chemistry, for the following reasons:

1. The active oxidant in Fenton’s Reagent is the hydroxyl radical ( $HO\cdot$ ) – a short-lived indiscriminant oxidant that is not likely to exhibit such high specificity to sulfide amidst the abundance of oxidizable organics present in untreated municipal wastewater.
2. Fenton’s Reagent typically requires a wastewater pH within the range of 2-5 in order to keep the  $Fe^{3+}$  dissolved – a higher pH results in Fe flocculation and a complete shutdown of free radical generation.
3. The levels of dissolved iron needed to efficiently generate hydroxyl radicals in wastewaters are typically  $> 10$  mg/L Fe; whereas, the level dosed into the Knott Interceptor during this PRI-SC study was about 3 mg/L Fe.

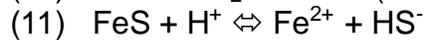
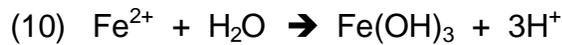
Relative to using iron salts (alone), the PRI-SC technology offers a number of benefits besides direct cost savings. These include reduced solids production, alkalinity loss, and salinity contribution (Figures 22 - 24).

In the case of solids production, equation (1) shows that 1.0 lbs-Sulfide will generate 2.8 lbs-FeS, assuming theoretical iron dosages. With solids handling/disposal costs of \$50 per ton, this can add 10% (or ca. \$0.07) to the actual cost per lb-Sulfide controlled.

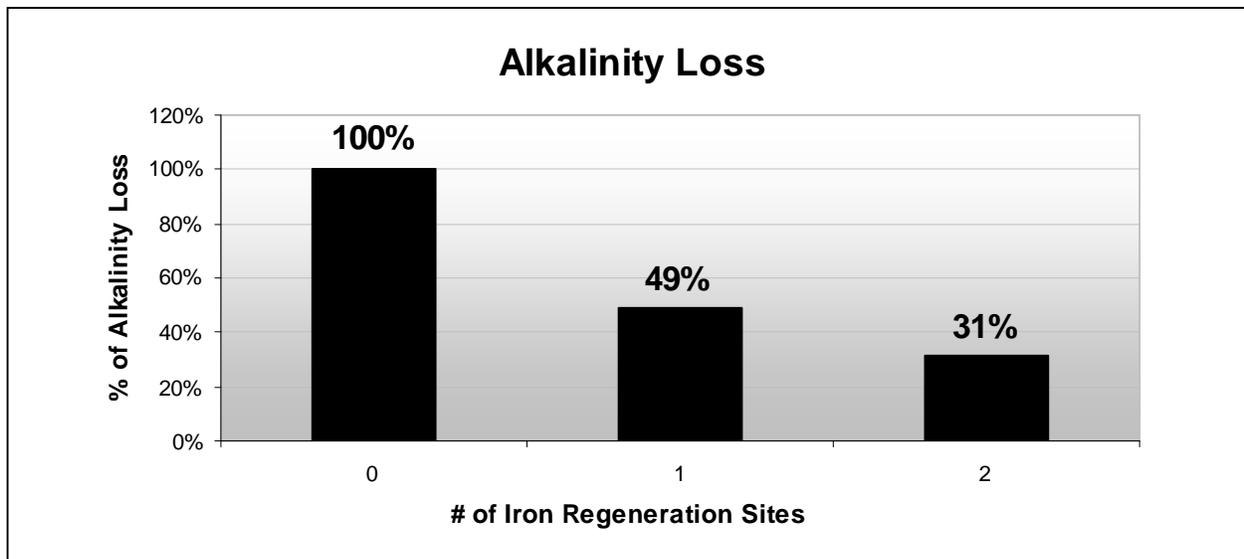
**Figure 22. Water quality impacts of PRI-SC versus  $FeCl_2$  alone: Solids production**



Iron salts also deplete alkalinity, which can be due to free acid in the product (typical spec is 1-4% free acid), FeS formation (per equation (1) = 2.1 lbs HCl per lb-Sulfide), and Fe<sup>2+</sup> hydrolysis (per equation (9) = 3 moles H<sup>+</sup> per mole Fe<sup>2+</sup>). Added together, the alkalinity loss can add up to > 3 lbs of CaCO<sub>3</sub> per lb-Sulfide controlled. The potential pH depression resulting from this loss may reduce the ability of iron to control sulfide to low levels by shifting the equilibrium in equation (10), and encourage volatilization of the remaining dissolved sulfide by shifting the equilibrium in equation (11). In this study, it was found that doubling the FeCl<sub>2</sub> charge at the upstream dose site depressed the wastewater pH by 0.4 units (pH 7.4 to pH 7.0), which was sufficient to shift the equilibrium from 30% of the dissolved sulfide present as H<sub>2</sub>S to 50% present as H<sub>2</sub>S. While this aspect is more relevant to low flow, high sulfide wastewaters, it can nonetheless require a lower dissolved sulfide target in order to achieve a given vapor H<sub>2</sub>S target.

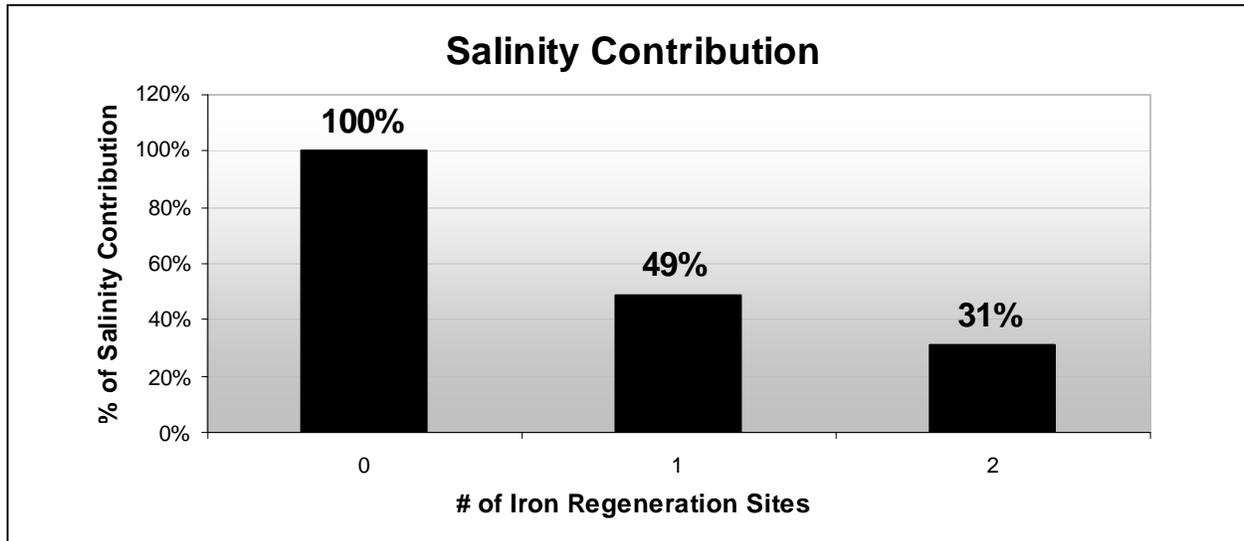


**Figure 23. Water quality impacts of PRI-SC versus FeCl<sub>2</sub> alone: Alkalinity loss**



Due both to the free acid content of the product and to the hydrolysis of FeCl<sub>2</sub>, chloride-based iron salts also add salinity to the wastewater (ca. 2 lbs of chloride per lb-Sulfide controlled, assuming stoichiometric doses). This issue is becoming increasingly important in the West as water re-use increases, particularly for irrigating agricultural crops.

**Figure 24. Water quality impacts of PRI-SC versus FeCl<sub>2</sub> alone: Salinity contribution**



There are other practical aspects of the PRI-SC technology that can prove useful in enhancing existing iron salt applications. For example, where iron is being used to control sulfides for several hours duration (thereby increasing the iron requirements), the feed rates can be reduced to control for a shorter duration, and H<sub>2</sub>O<sub>2</sub> can be added prior to the discharge to oxidize the remaining sulfide. In this way, residual sulfide levels of < 0.1 mg/L are afforded within 1-2 minutes – something that is not afforded by either chemical alone even at 2-4 fold excess doses. Further, if this discharge were into the headworks of a treatment plant, the resultant free (hydrous) ferric oxide will enhance sulfide control through the primary clarifiers and into downstream thickeners and/or digesters.

## **CONCLUSIONS**

This study has shown that it is cost-effective to supplement with H<sub>2</sub>O<sub>2</sub> those chemical programs using iron salts for sulfide control and enhanced clarification. The combination of FeCl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> as employed in the PRI-SC technology affords improved performance and lower iron consumption, while providing significant economic benefit. Large municipalities that currently use iron salts for these purposes may find the results particularly helpful in improving operations and hedging iron costs. Municipalities currently practicing either (but not both) enhanced clarification or sulfide control may now find that they can fund both operations through their existing budget.

The objectives of this study were met by showing:

1. The concept of PRI-SC technology (i.e., regeneration by H<sub>2</sub>O<sub>2</sub> of spent FeS to ferric iron) was evidenced by the following upon H<sub>2</sub>O<sub>2</sub> addition: 1) removal of Total Sulfide (predominantly FeS); 2) conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup> (per analyses); 3) removal of sulfide mass twice the amount otherwise theoretically afforded by FeCl<sub>2</sub> alone; and

- 4) reduction of least one-half the  $\text{FeCl}_3$  use at the treatment plant with no loss in clarification effectiveness.
2. The PRI-SC technology successfully controlled sulfide levels through the length of the interceptor to 0.5 mg/L dissolved sulfide and 25 ppm vapor  $\text{H}_2\text{S}$ , representing reductions of about 95%. The effective treatment cost excluding plant credits was about \$1.00 per lb-sulfide controlled. The net effective treatment cost considering the reduced amount of  $\text{FeCl}_3$  needed for enhanced clarification was about \$0.50 per lb-sulfide controlled, which is substantially less than that of either chemical used alone.
3. It was further shown that 85-90% 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 influent  $\text{Fe}^{2+}$  in this study (to provide  $\text{Fe}^{3+}$ ) was less than the purchase price of  $\text{FeCl}_3$ , thus affording the opportunity to relocate additional  $\text{FeCl}_3$  credits to the collection system program.

## ACKNOWLEDGMENTS

Richard Winkler contributed much to the operational aspects of the study, as did his staff in performing the field sampling and maintaining the equipment.

## REFERENCES

- Fenton, H. J. H (1894) The oxidation of tartaric acid in presence of iron. *J. Chem. Soc. Proc.*, **10**, 157.
- Kang, S. F; Yen, H. Y. (1995) Reduction of Trihalomethane Formation using Ferrous / Hydrogen Peroxide. *Water Supply*, **30** (3/4), 53.
- Watts, R. J., et.al. (1990) Treatment of Pentachlorophenol-contaminated soils using Fenton's Reagent. *Haz. Waste and Haz. Mater.* **7**, 335.

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