



Sulfide Characterization Study

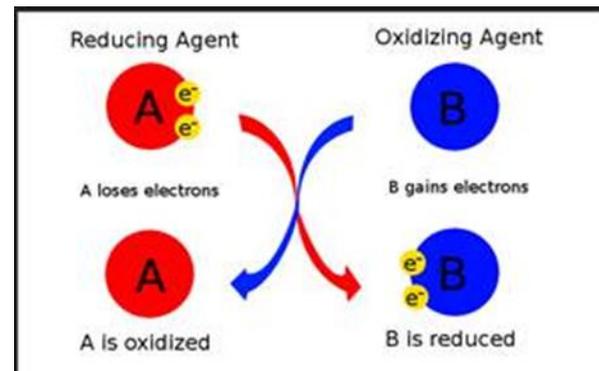
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Pretreatment Program
10/25/2018

Introduction

- ▶ Hydrogen sulfide is one of the leading causes of workplace gas inhalation deaths in the United States.
- ▶ According to the Bureau of Labor Statistics, hydrogen sulfide caused 60 worker deaths between 2001 and 2010 (OSHA).

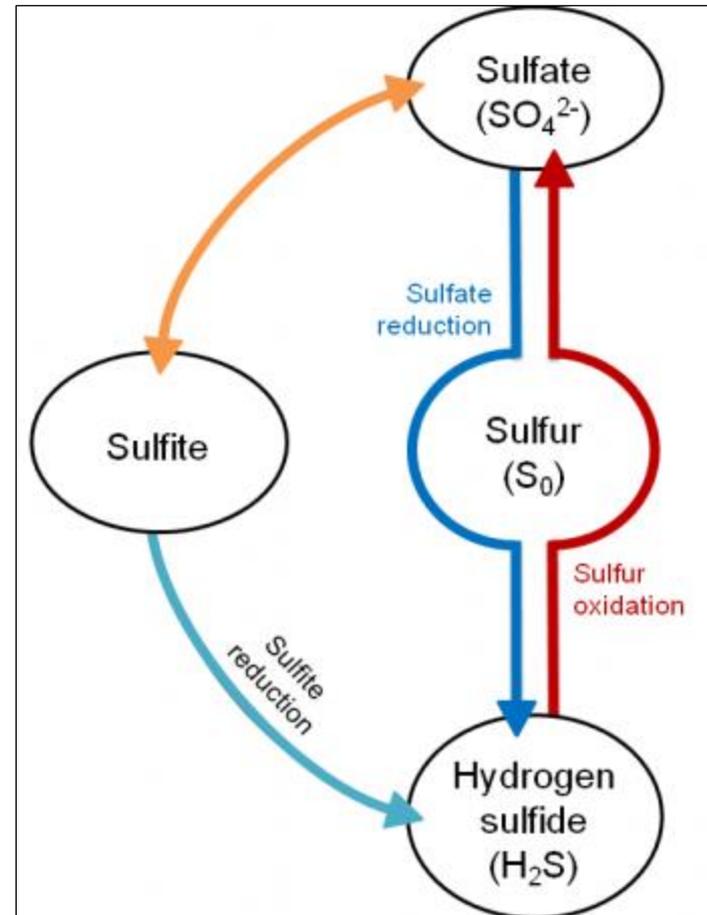
Sulfide Chemistry

- ▶ Oxidation is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion.
- ▶ Reduction is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.
- ▶ A reducing agent, loses electrons and is oxidized in a chemical reaction.



Sulfur Cycle

- ▶ As indicated in the diagram, under anaerobic conditions sulfate is reduced to sulfite and sulfide.



Wastewater

The composition of Wastewater (WW) characteristically contains sufficient ionic strength, temperatures below 20°C, and a composition of chemical and biological contaminants. Depending on the location in the Wastewater Treatment Plant (WWTP)—influent, aeration basin, nitrification/denitrification, effluent—samples can show different ORP values.

While the influent often comes with ORP readings around -200 mV, the WW stream changes the ORP to positive values of around +50 mV due to oxidation of the reducing species.

ORP [mV]	Process
-280...-150	Development of methane
-200...+100	Reduction of sulfate
+180...+400	Reduction of iron
+220...+500	Reduction of manganese
+300...+600	Reduction of nitrate

Table 3: Typical ORP values of WW in a WWTP

Source: Dr. Axel W. Bier, Hach-Lange, Application Specialist, "Introduction to Oxidation Reduction Potential Measurement," October 28, 2009. HACH Website <http://www.hach.com/asset-get.download.jsa?id=7639984590>

Sulfide Oxidizing Bacteria

- ▶ Sulfide can be biologically oxidized to elemental sulfur with *Thiobacillus* sp. in the presence of oxygen or *Thiobacillus denitrificans* in the presence of nitrate or *Chlorobium limicola* in the presence of sunlight.
- ▶ The *Thiobacillus denitrificans* can utilize nitrate with the formation of N_2 as an electron acceptor.
- ▶ The oxidation can possibly further continue to form the sulfate ion.

Problem Statement

- ▶ Industry has consistently exceeded the screening level for sulfide of 1 mg/l.
 - Sulfide concentration up to 16 mg/l.
- ▶ Industry has consistently exceeded the screening level for sulfide of 2 mg/l.
 - Sulfite concentration up to 28 mg/l.
- ▶ In accordance with Town of Merrimack Code §158-39 (K), *Limited Discharges; enforcement*, the facility is required to implement, within thirty (30) days of receipt of the repeat analyses, a study to evaluate the potential impact of the discharge of this pollutant to the Town collection system, and the wastewater treatment facility.

Impact to Wastewater Facility

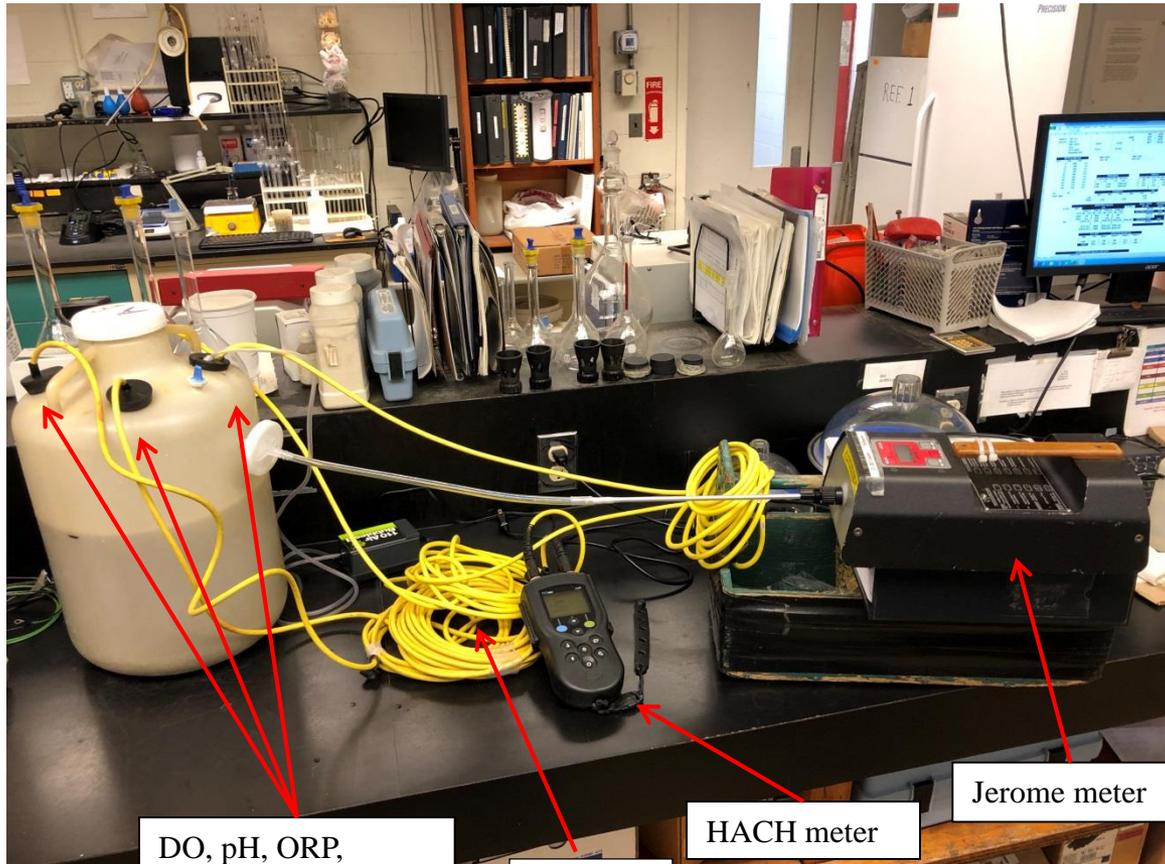
▶ Health & Safety

- [29 CFR 1910.1000 TABLE Z-2](#), Toxic and hazardous substances Exposures must not exceed 20 parts per million (ppm) (ceiling) with the following exception:
 - If no other measurable exposure occurs during the 8-hour work shift, exposures may exceed 20 ppm, but not more than 50 ppm (peak),
 - For a single time period up to 10 minutes.
- ACGIH recommendation for an 8 hour time weighted average of 1 ppm.

▶ Sewer System infrastructure:

- There was corrosion at the facility discharge flume.
- The flume was rehabilitated and it was epoxy coated because of the excessive corrosion.

Procedure

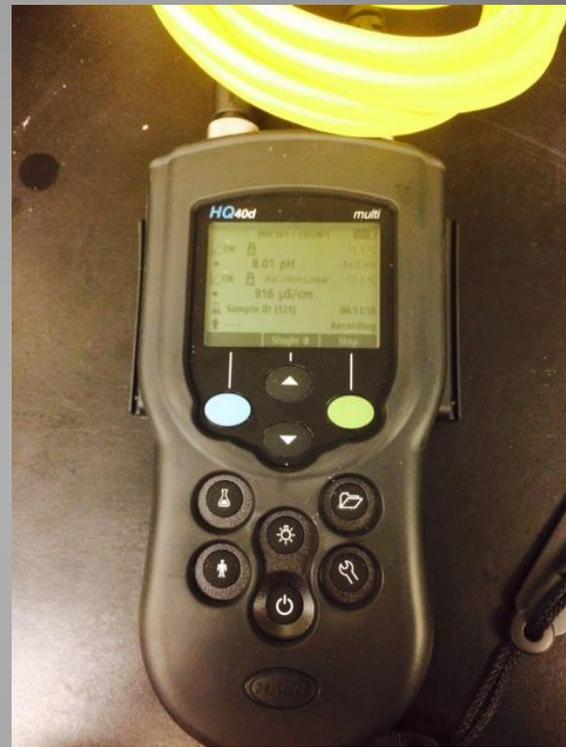
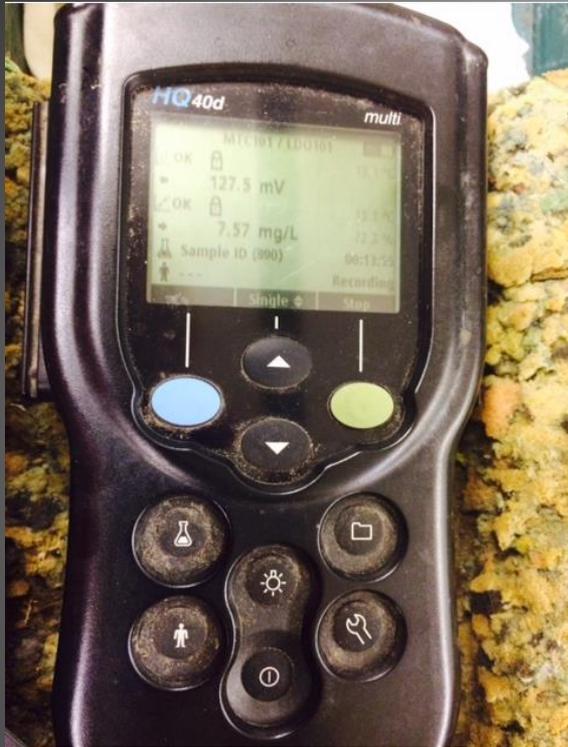


– Collected a twelve liter grab sample from Industry wastewater from their effluent pump station

– Monitored the water for hydrogen sulfide gas, dissolved oxygen (DO), pH, oxidation reduction potential (ORP), conductivity

– Measure before and after sulfide concentration with HACH spectrophotometer

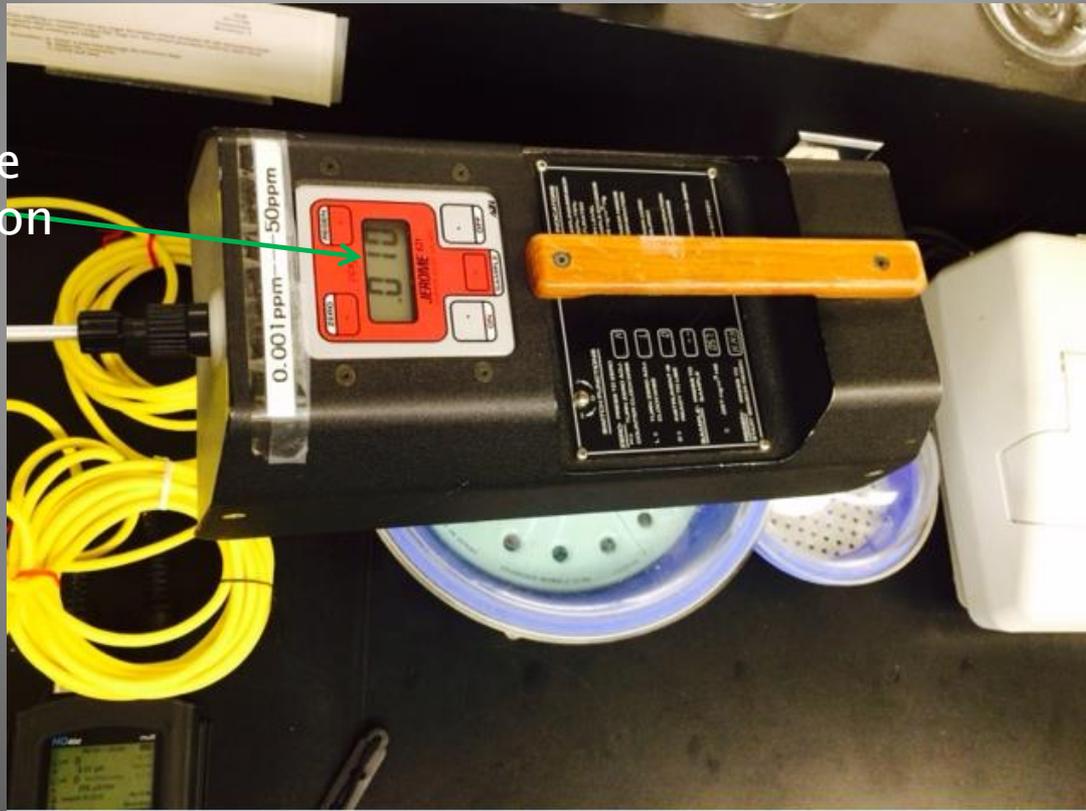
Meter Outputs



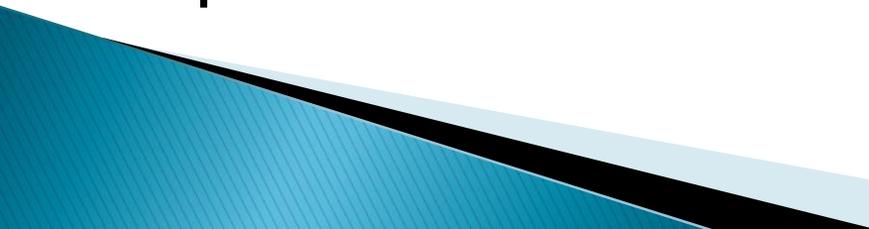
Each meter continuously logs data which can be downloaded into excel.

Jerome Meter

Hydrogen sulfide
Gas Concentration

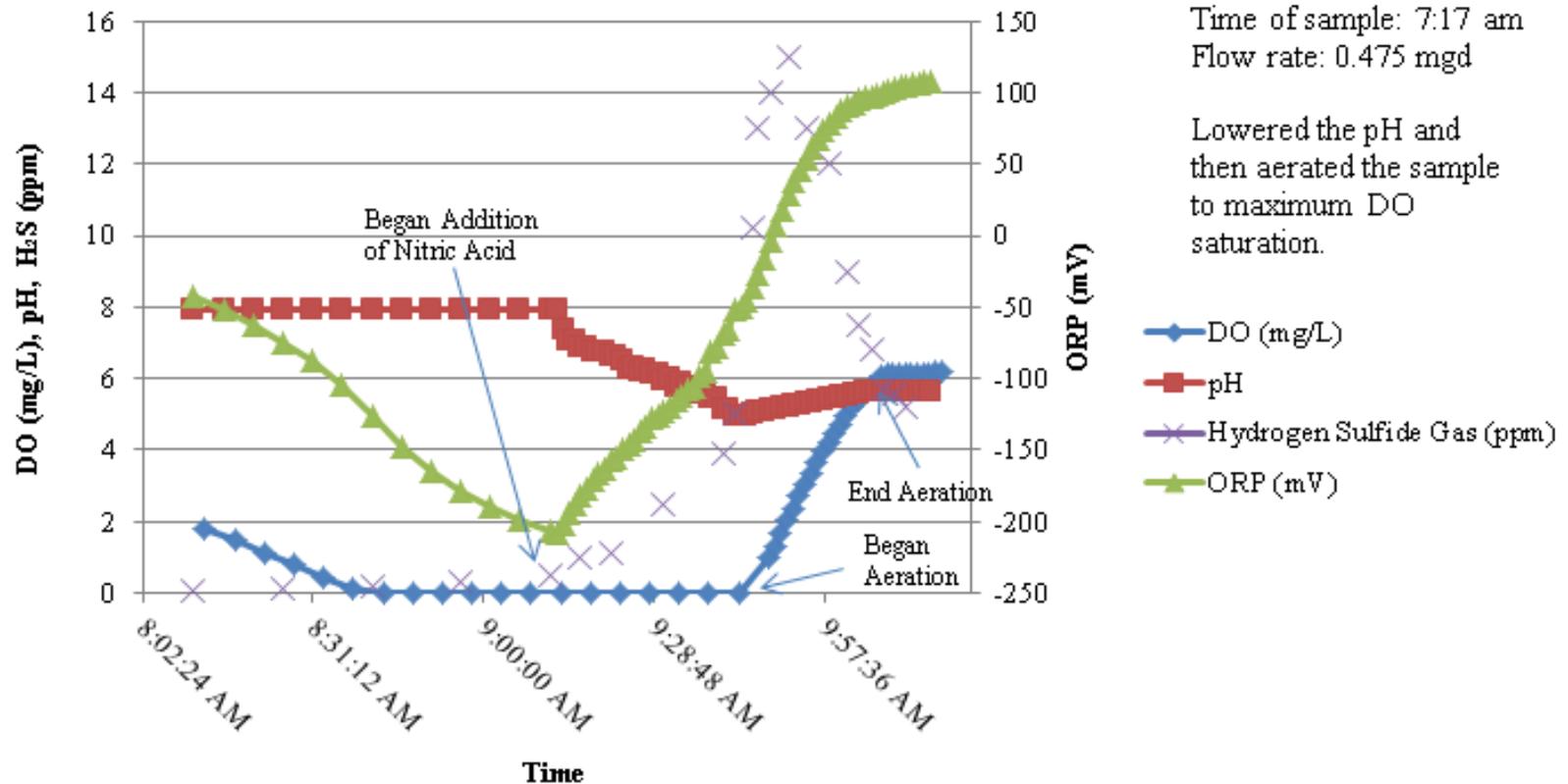


Issue

- ▶ Currently industry is not adequately aerating their wastewater.
 - ▶ When their wastewater comes to the plant and mixes with the other incoming wastewater the pH can drop.
 - ▶ The wastewater then is aerated at the treatment plant and hydrogen sulfide can be produced.
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Results

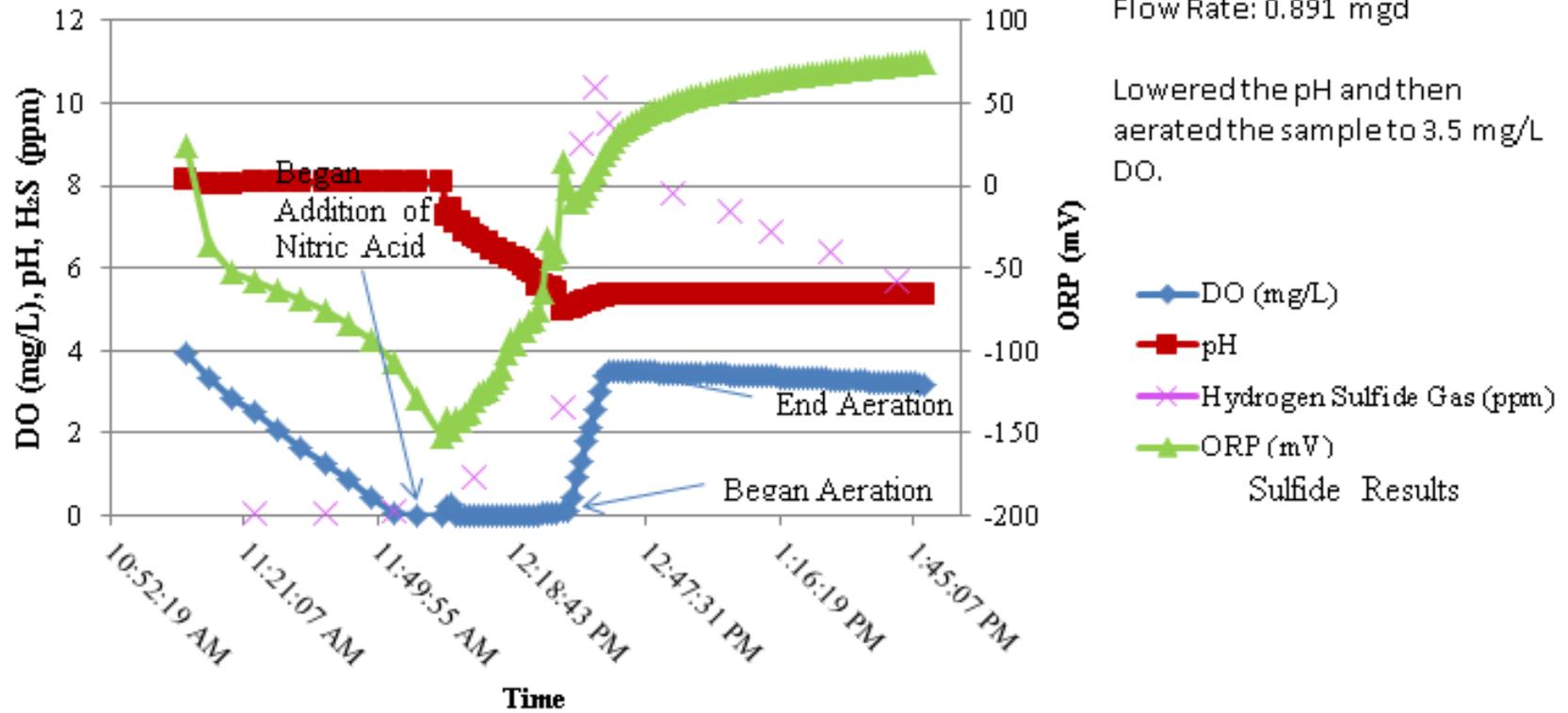
June 29, 2018 Sulfide Characterization Study Results-2



August 3, 2018 Sulfide Characterization Study Results-2

Time of Sample: 10:51 am
Flow Rate: 0.891 mgd

Lowered the pH and then aerated the sample to 3.5 mg/L DO.

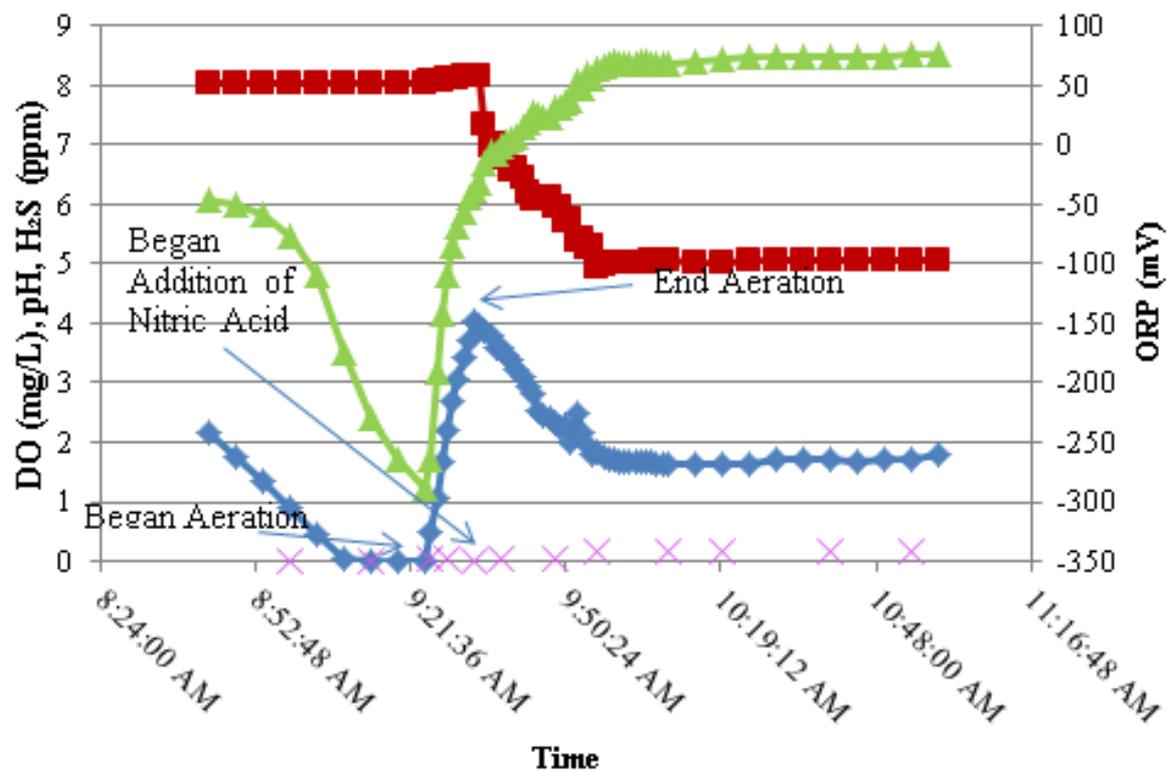


Sulfide Results

July 18, 2018 Sulfide Characterization Study Results-1

Time of Sample: 8:15 AM
Flow Rate: 1.206 mgd

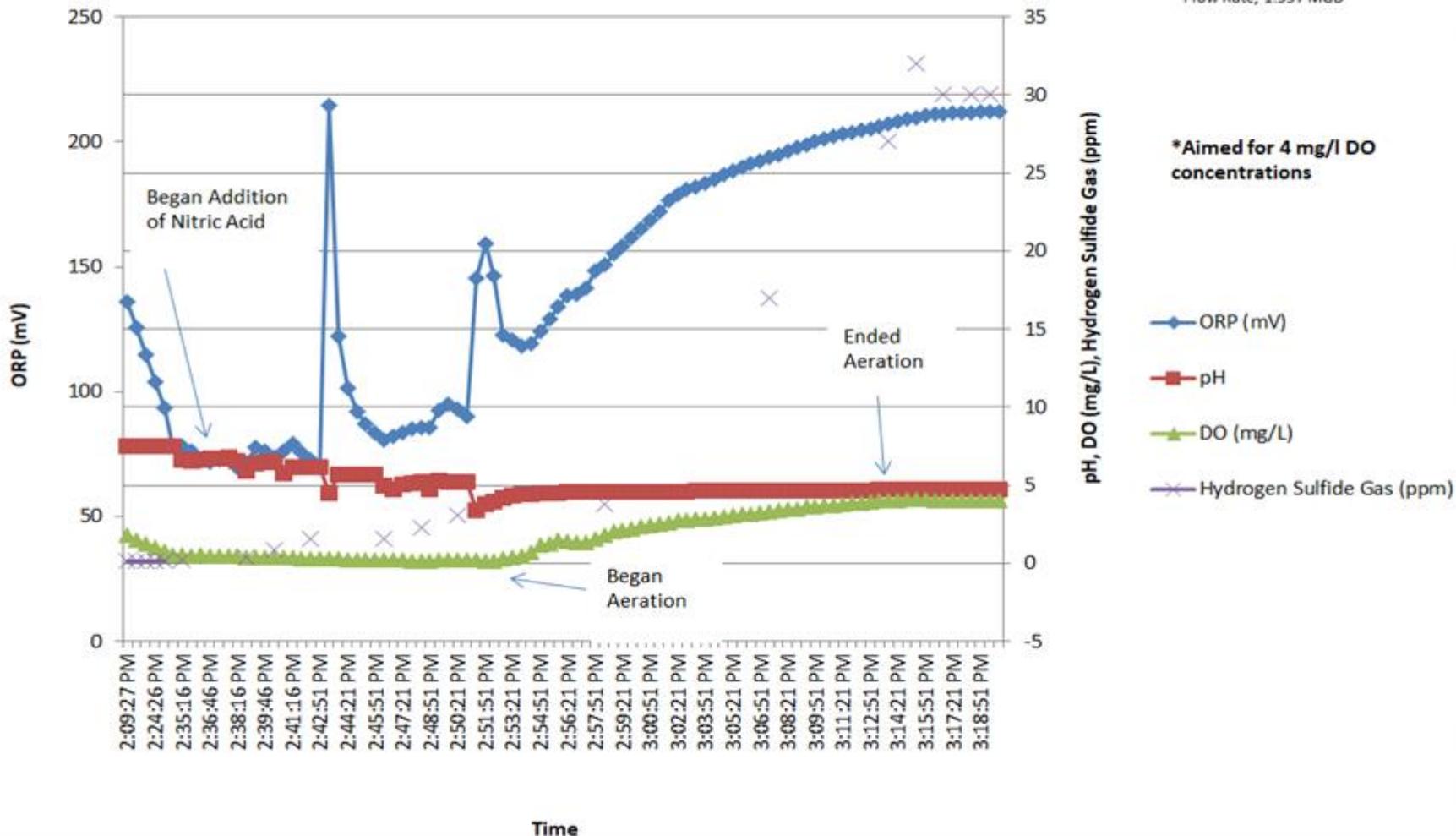
Aerated the sample to 4 mg/L
DO and then lowered the pH.



- ◆ DO (mg/L)
- pH
- × Hydrogen Sulfide Gas (ppm)
- ▲ ORP (mV)

August 15, 2017 DO Characterization Study Results

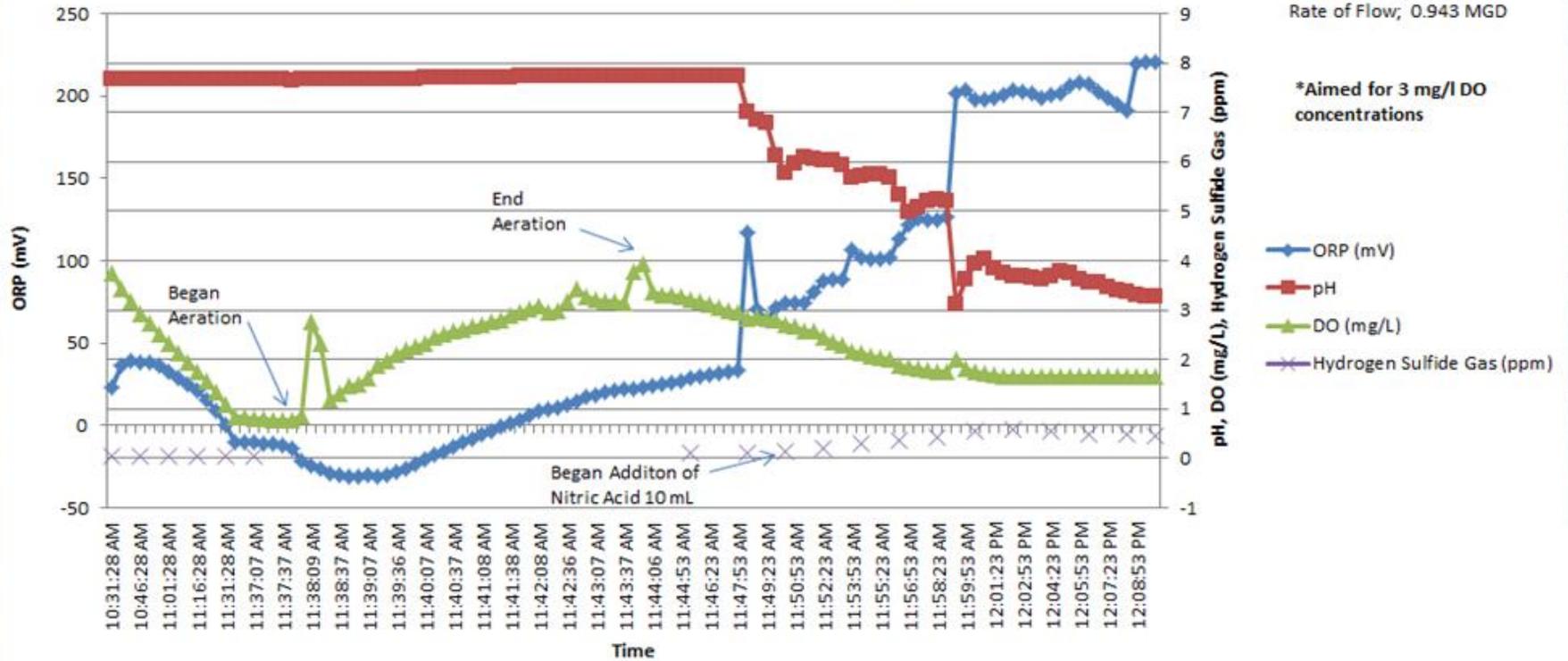
Time of Sample; 1:23 PM
Flow Rate; 1.597 MGD



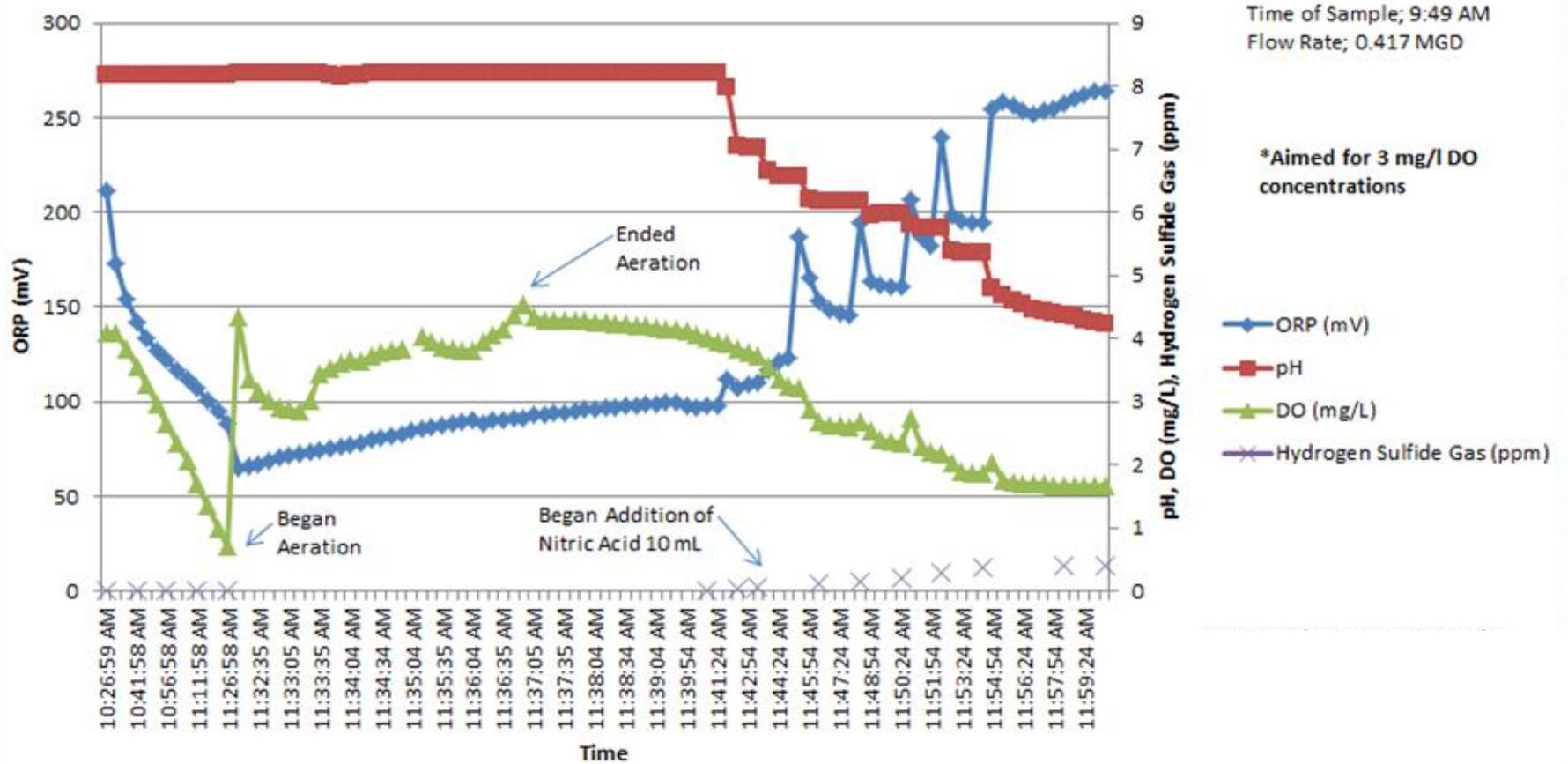
JULY 14, 2017 DO Characterization Study Results

Time of Sample; 9:56 AM
Rate of Flow; 0.943 MGD

*Aimed for 3 mg/l DO concentrations



July 07, 2017 DO Characterization Study Results



2018 – Aerating Prior to Dropping pH Results

Results when aerating first ranged from .0046–2.4 ppm.

Target DO (mg/L)	Average Maximum H ₂ S Produced(ppm)	Number of Runs
3.0	2.00	1
3.5	1.55	4
4.0	1.39	2
5.0	1.30	1

2018 –Aerating After to Dropping pH Results

Results when dropping the pH first ranged from 1.9–20 ppm.

Target DO (mg/L)	Average Maximum H ₂ S Produced (ppm)	Number of Runs
3.5	11.3	4
4	1.9	1
5	15.0	1
Saturation	8.7	2

Results

- ▶ Occupational Safety and Health Administration (OSHA) has an 8 hour work limit for hydrogen sulfide gas of 10 ppm and 20 ppm ceiling value.
 - ▶ American Conference of Governmental Industrial Hygienists (ACGIH) recommends an 8 hour work limit of 1 ppm.
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Results

- ▶ As pH was lowered, hydrogen sulfide production increased.
 - ▶ The Industry current pH limit is 5.0–9.5.
 - ▶ pH ranged from 7.89–8.20 for our 16 runs.
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Conclusion

- ▶ Raising the pH limit will also help decrease the chance of hydrogen sulfide gas.
 - ▶ Adding aeration to the pretreatment process will result in a much smaller chance of hydrogen sulfide production at the treatment plant.
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Conclusion

AB effluent does not impact the Town collection system, WWTF, or health and safety of Town employees under the following effluent conditions:

- ▶ Effluent pH greater than 5.0.
- ▶ Dissolved Oxygen greater than 5.0 mg/l.
- ▶ ORP Monitor Only – 50 mV.
- Dosage Ratio ppm of FeCl_2 to ppm H_2S (in solution) is maintained at a level that ensures that all sulfide is reacted to generate FeS^- .