Odor Control in Collection Systems

2012

OWEA Annual Conference

Who is Weatherford Engineered Chemistry ?

- A division of Weatherford International
- Primarily servicing the industrial market, oil and gas business, and waste water treatment industries
- Three ISO 9001 registered plants and one ISO 14001 registered plant

Weatherford, Pittsburgh

Weatherford, San Antonio

Weatherford, Newburgh, IN

Weatherford, Canada

Core Business

- Engineered Chemistry
- Hydrogen Sulfide Gas Removal
- Oil and Gas Services
- Plant Air Moisture Reduction

Locations

- Manufacturing facilities located in Pittsburgh, PA, San Antonio, TX, Odessa, TX, Newburgh, IN, and Red Deer, Alberta
- Support offices in Pittsburgh, Orlando, Houston, Calgary, Moscow, Dubai, and Rio de Janeiro, Beijing, and Argentina

What is H_2S?

- Hydrogen sulfide is a corrosive, poisonous gas
  - Heavier than air
  - Rotten egg odor at low concentrations - <100ppm
  - Burns with a blue flame to produce SO_2

H_2S Sources

- Natural occurring in oil & gas reservoirs – ppm levels to high % range
- H_2S forms from the activity of sulfate reducing bacteria.
  - Under anaerobic conditions, the sulfate ion is used as a source of oxygen for respiration by some bacteria
- Water phase, including waste water processing, water disposal wells, etc.

Where is H_2S

- Generated in Subterranean Foundations
  - Potable Drinking Water
  - Natural Gas
  - Crude Oil
- Sewage Plants
  - Liquid
  - Vapor
- Landfills

H_2S Toxicity

0.13 ppm	minimal odor
4.60 ppm	moderate identifiable odor
10 ppm	initial eye irritation
27 ppm	strong odor
100 ppm	coughing, loss of sense of smell after 2-5 minutes
200-300 ppm	eye inflammation respiratory tract irritation
500-700 ppm	loss of consciousness and possible death in 30 min. to 1 hr
700-1000 ppm	rapid unconsciousness, *death*

Treatment

- Liquid scavenger
  - Polymeric Amine Chemistry
  - Iron Salts
- pH Control
- Oxidation
- Alternative food sources for the SRB bacteria

What is Polymeric Amine Chemistry

- Patented technology that safely and effectively removes H_2S
- Twenty year old technology used in the oil & gas industry
- Polymeric Amine Condensate converts sulfide to a Polyamine Sulfide
- Used in Scrubber Towers, Bubble Towers, Static Mixers, Absorption Towers, and Collection Systems
- Introduced by single or multiple injection points by atomization and drip feeding

Polymeric Amine Chemistry

- Non-Hazardous
- Non-Flammable
- Freeze point in excess of -20F
- No special storage considerations

Why Use Polymeric Amine Chemistry

- Efficient and cost effective way to remove H_2S
- Reacts to form a corrosion inhibitor
- Reduces maintenance costs
- Reduces solids build up
- Environmentally friendly
- Ease of handling
- Methyl, ethyl, & diethyl mercaptan removal

Polymeric Amine Chemistry in Liquid Phase

- Is a true scavenger
- H_2S will not reoccur
- Reacts into a semi-polymer
- Chemistry can withstand temperatures as low as -20 F without viscosity and freezing problems
- Is selective only to H_2S methyl, ethyl & diethyl mercaptan
- Needs turbulence to be effective
- Works best in forced mains or prior to the suction side of the pump going to a sludge holding tank
- Will remove odors in collections, wet scrubbers, and belt press rooms
- Will not work well in a gravity main
- Testing is in progress to make the molecule proactive

Polymeric Amine Hybrid

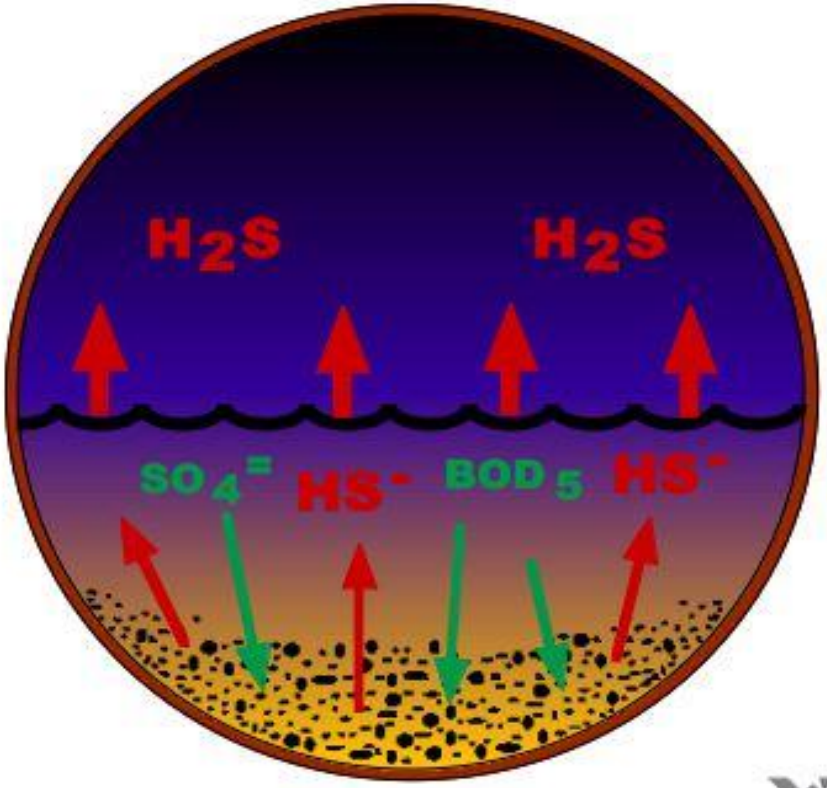
- Both Water and Oil Soluble
- All the same characteristics as polymeric amine chemistry
- In the oil phase attacks H_2S in the Slime Layer
- Water Soluble is polymeric amine
- Twice the cost
- Above 30 GPD in a Collection System
- One Test Location went from 19 GPD to 2 GPD

Spent Solution
example hazards analysis

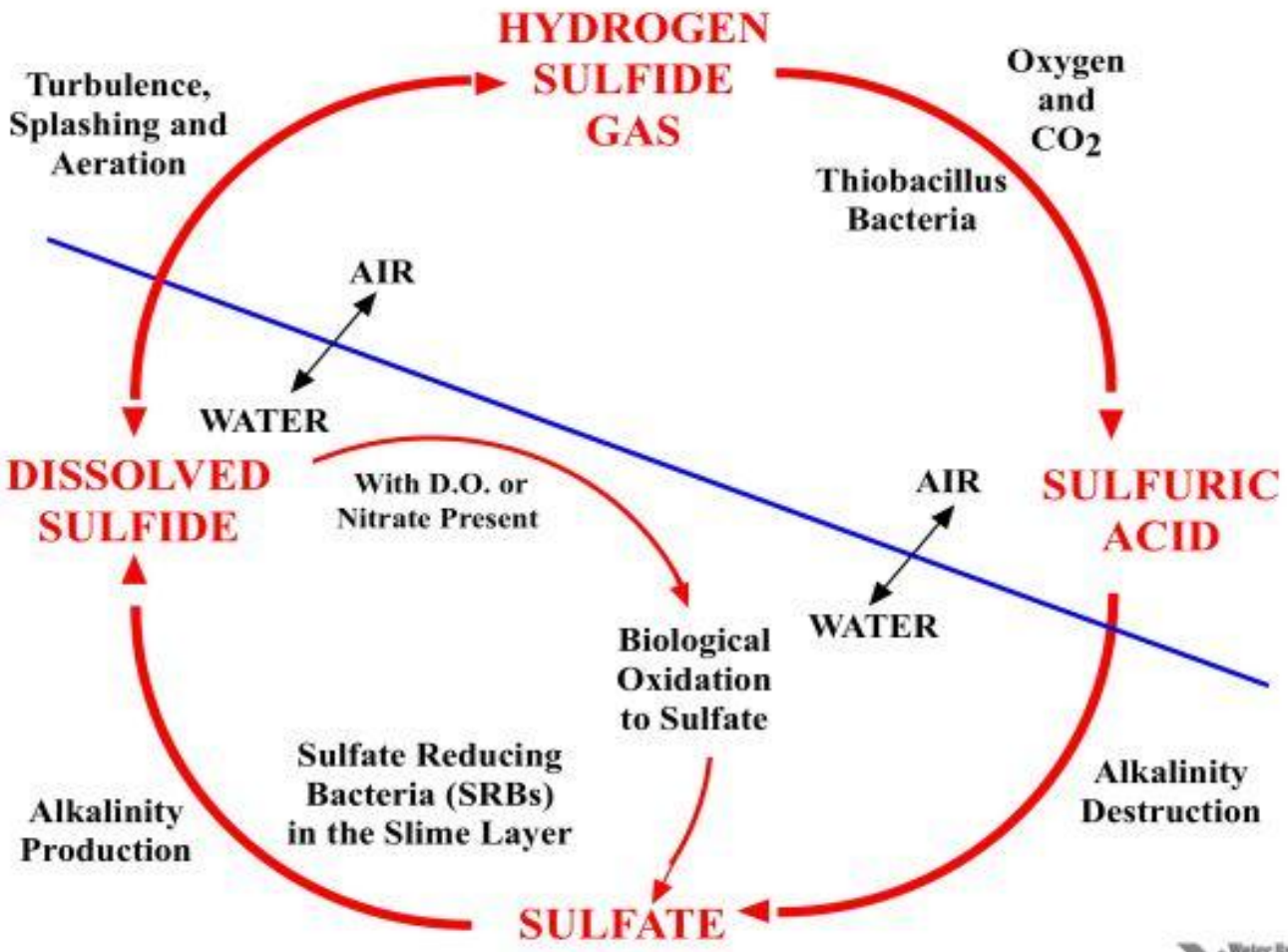
	Results	Limit
Flammability:		
Flash pt ^{0}F	>212	>140
Corrosivity:		
pH	7.0	<2 or >12.5
Reactivity:		
Sulfide	nonreactive	500ppm
Cyanide	nonreactive	250ppm
Metals	no heavy metals or halogens	

Sewer Debris Increases Sulfide Production

All Surfaces Below the Waterline in a Sewer Grow a Slime Layer. Debris in a Sewer Provides Additional Surface Area Upon Which to Grow Sulfate-Reducing Organisms, thus Increasing the Rate of Sulfide Generation.



The Sewer Sulfide Cycle



Collection Systems

Collection Systems

- H2S Reduction
- Mercaptan removal
- Corrosion Inhibitor
- Odor Control

Treatment Procedure

- **Determine H_2S Levels**
  - Gastec Sulfide Detection Tubes in Liquid
  - Odalog Gas Detector in Vapor
- **Begin Drip Feeding Polymeric Amine Chemistry**
  - GPD x ppm H_2S /1,000,000 x 4 = GPD
  - 500,000 x 8 = 4,000,000 x 4 = 16 / 24 = .67 GPH

Results

- Reduction in H_2S Levels
- Reduction in Odor Complaints
- Reduction in Solids Build-up
- Reduced Corrosion

Case Study Hermitage, Pa.

- Resident was complaining of offensive odor
- He and his wife were experiencing headaches
- Odor source was isolated to bathroom
- Specifically the toilet
- Source was traced to a forced main located adjacent to residents house

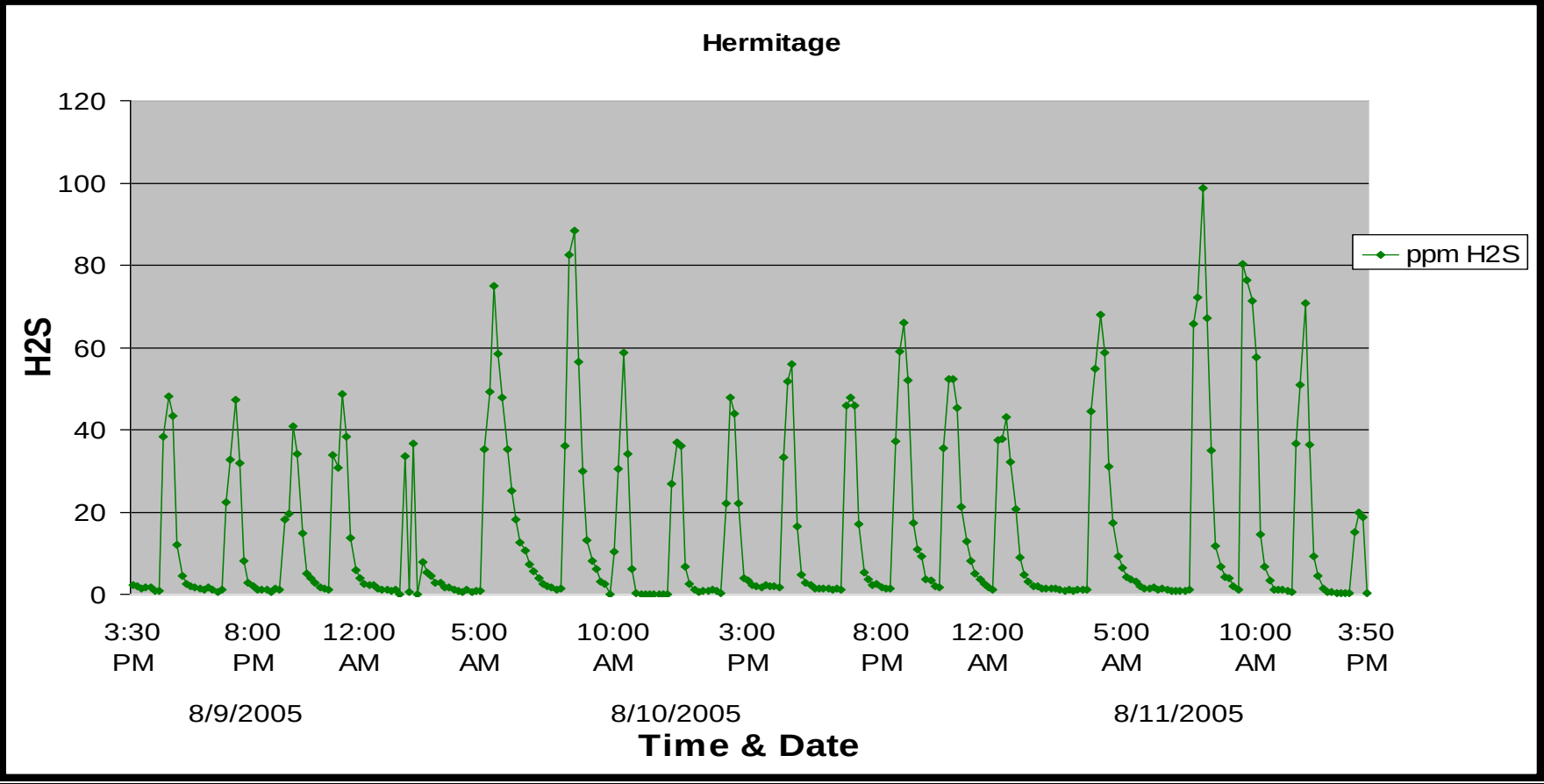
Case Study City of Hermitage, PA

- **This trial was conducted under the supervision of *Hickory Engineering* to test the performance of polymeric amine chemistry for removal of H_2S in collection systems.**
- **First action was to install a vent stack to eliminate odor.**
- **This proved to be unsuccesfull.**

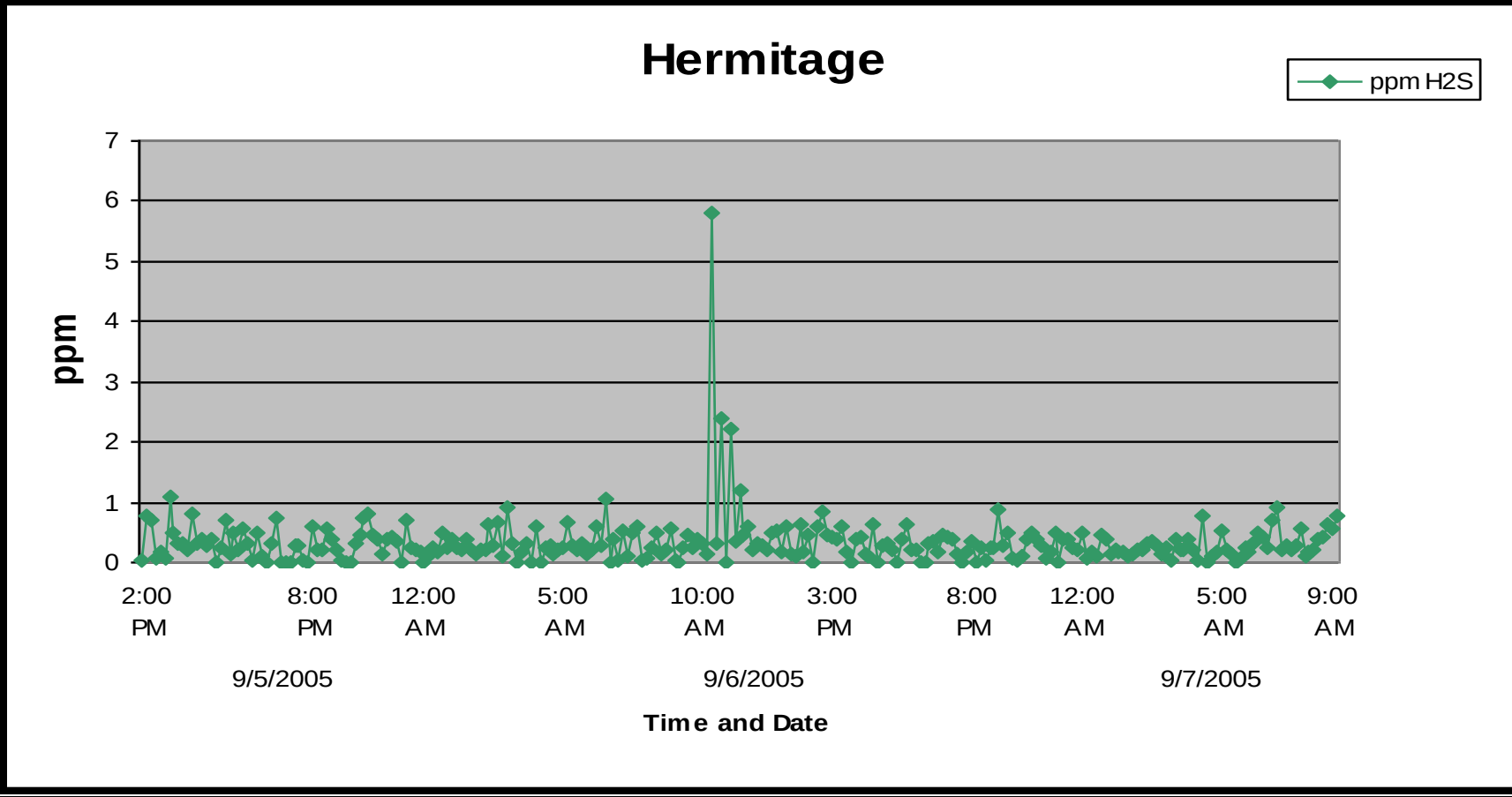
Treatment with Polymeric Amine Chemistry

- **Flow rates and H_2S levels were determined**
- **Flow rates and H_2S levels are used to determine dosage of any chemistry for H_2S & mercaptan removal**
- **Started dosing at the rate of 5 GPD with polymeric amine chemistry**
- **Levels were reduced from 100 ppm to less than 4 ppm H_2S in vapor**

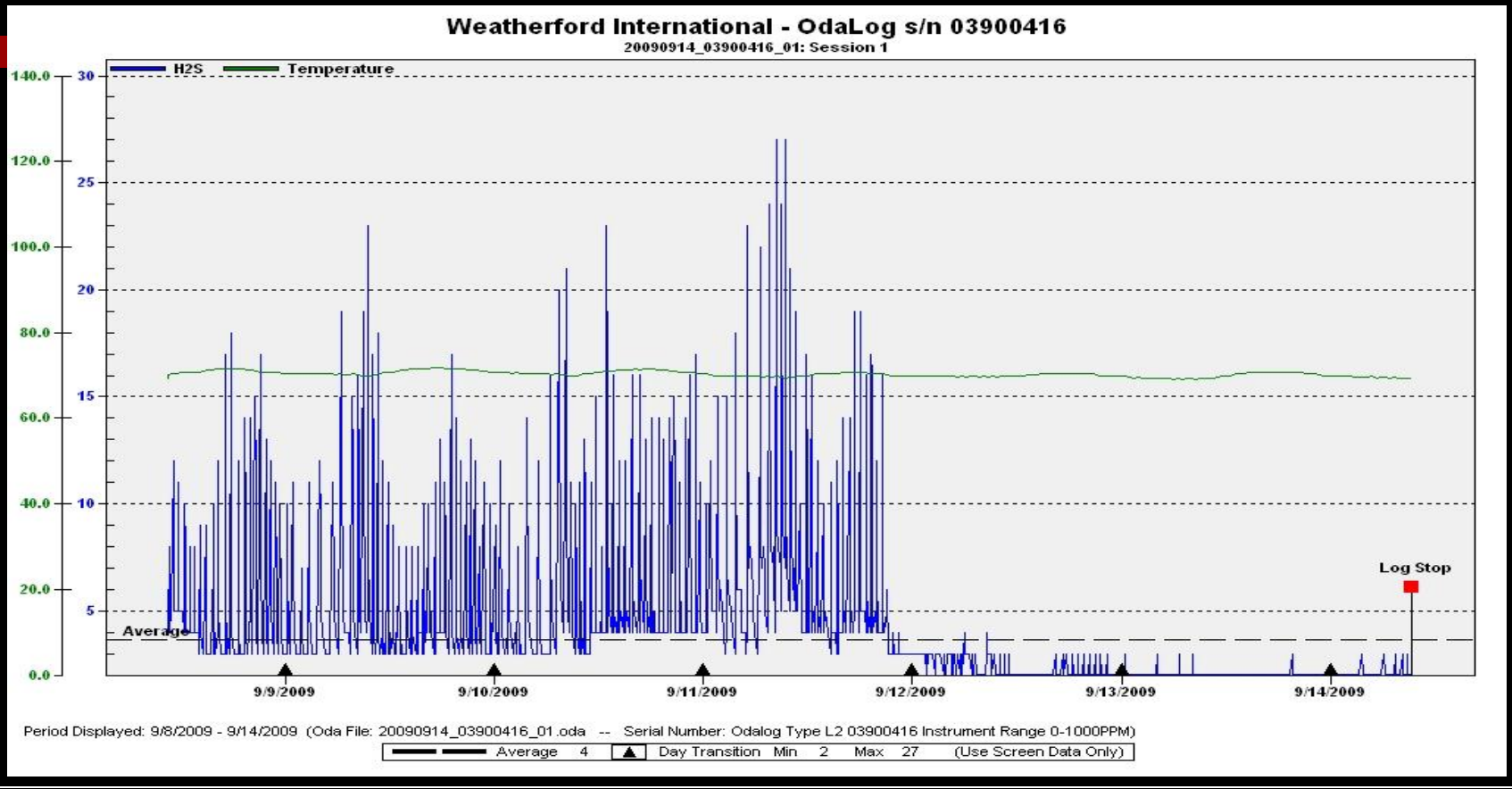
Before treatment



After treatment



Sample Rd. Hermitage, Pa.



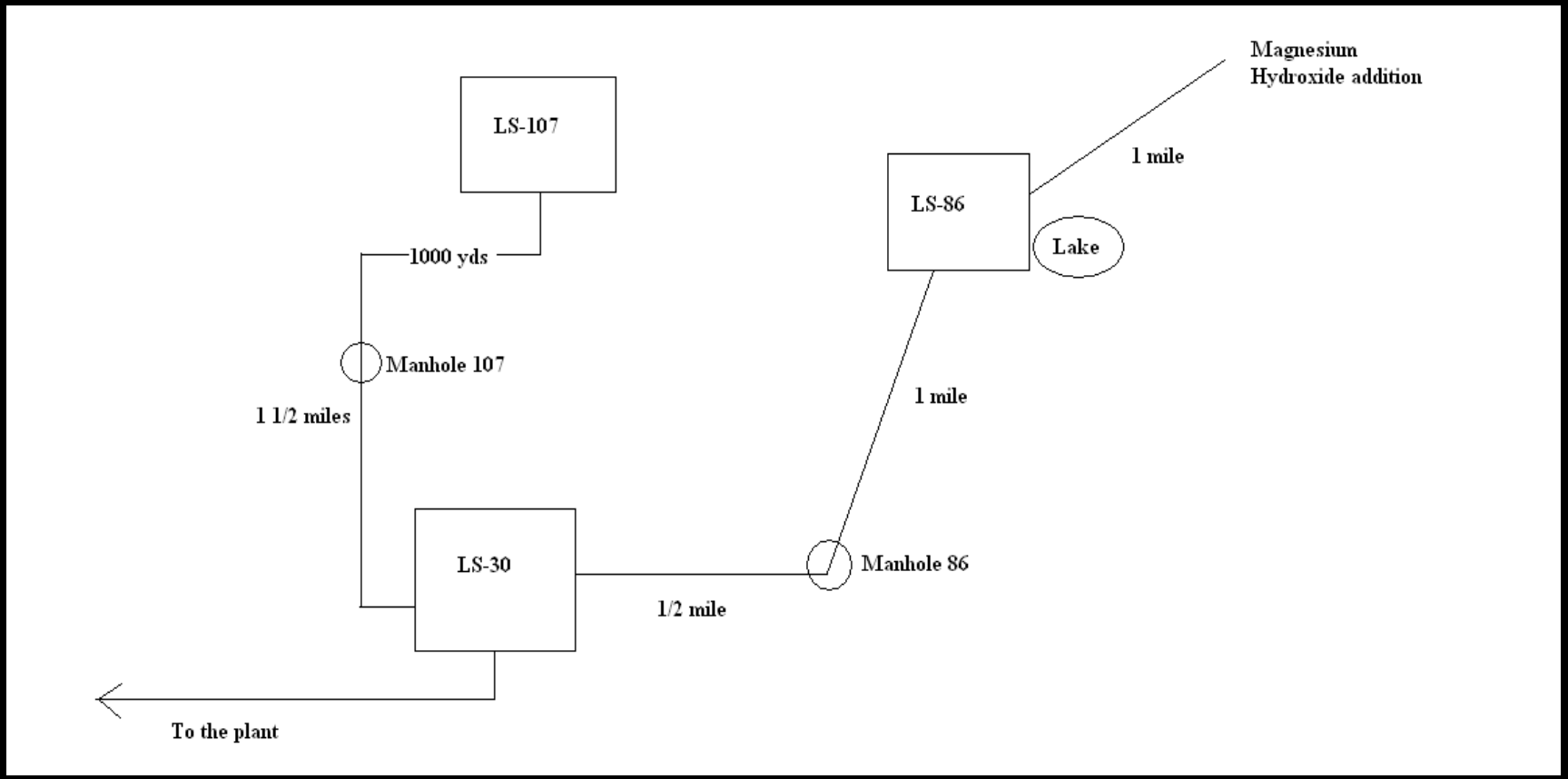
Corrosion Rates

- Comparison with & without polymeric amine chemistry
- Two similar lines 350,000 GPD Flow Rate
- 4-6 ppm Dissolved Sulfides
- No treatment 9 mills plus annual metal loss
- Treated line less than 1 mill annual metal loss
- Analysis was taken in Hermitage, PA.

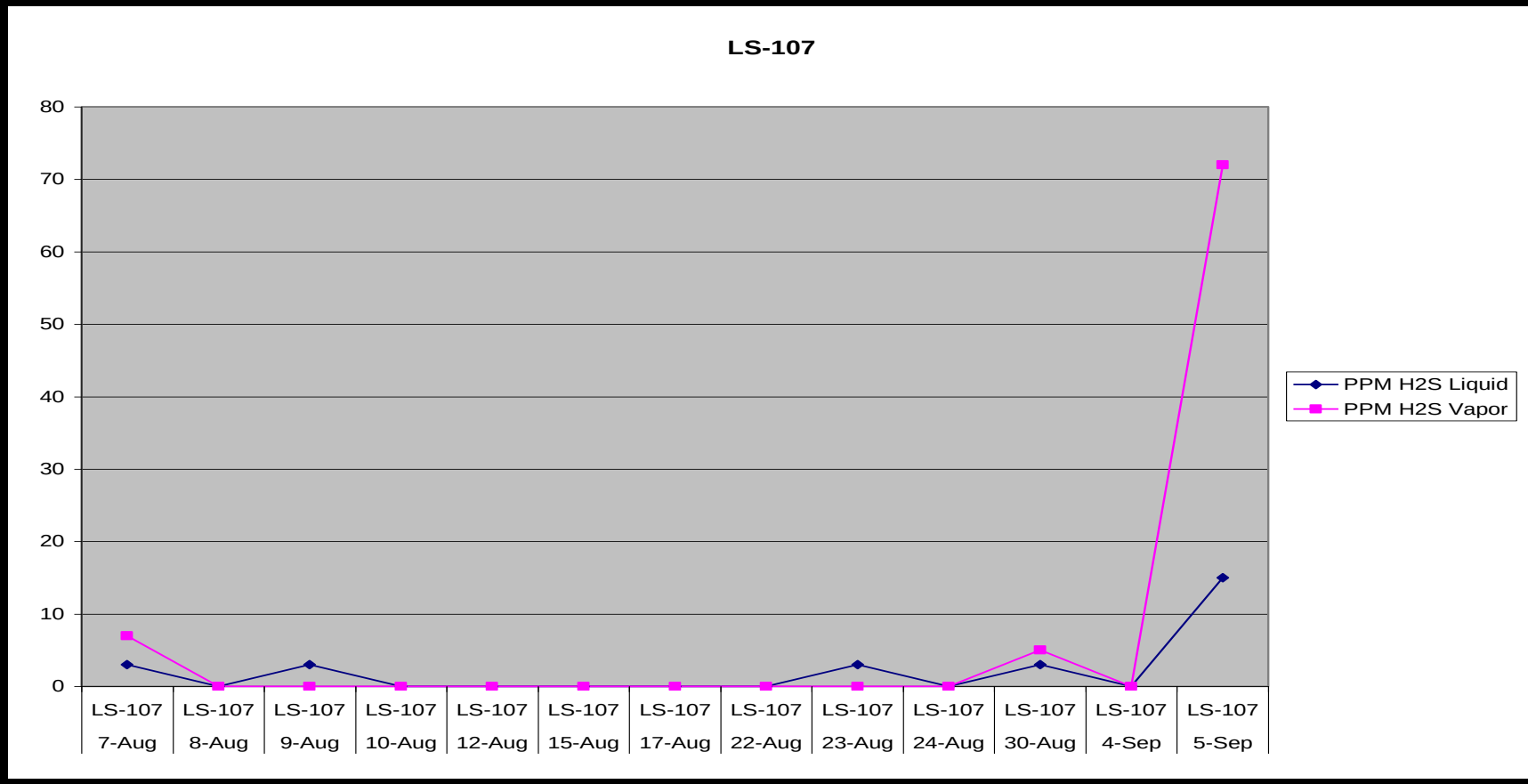
Case Study #2 Summit County

- Treatment trial at LS-107 & LS-86
- Recurrence of H_2S downstream of LS-107 to LS-86 treating with magnesium hydroxide.
- Sampling was taken daily during trial period
- Both liquid and vapor samples were taken
- Sampling was also conducted by Ben Duke, Summit County
- Summit County has converted these location to polymeric amine chemistry from the usage of magnesium hydroxide

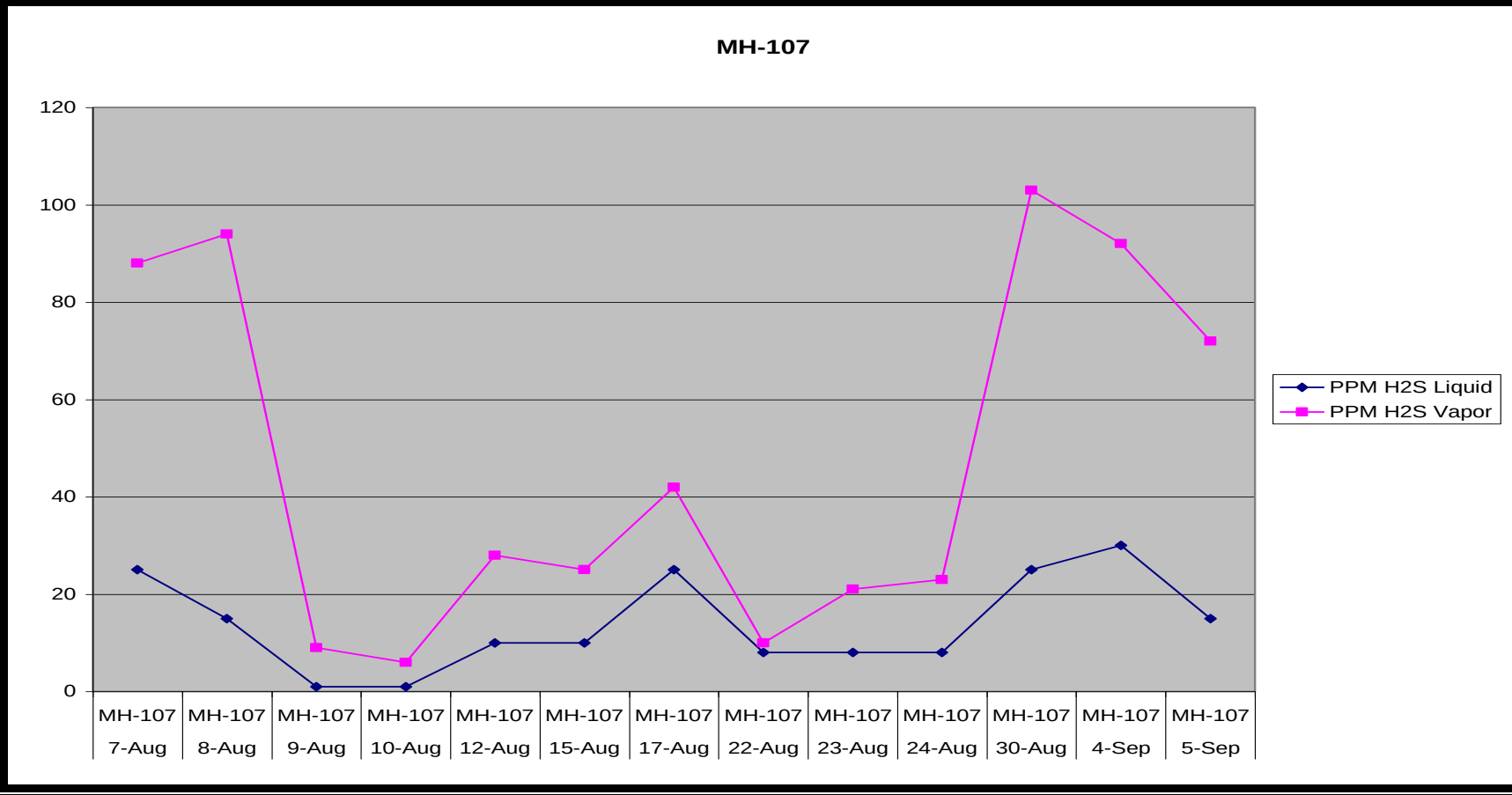
Flow Chart Summit County Trial



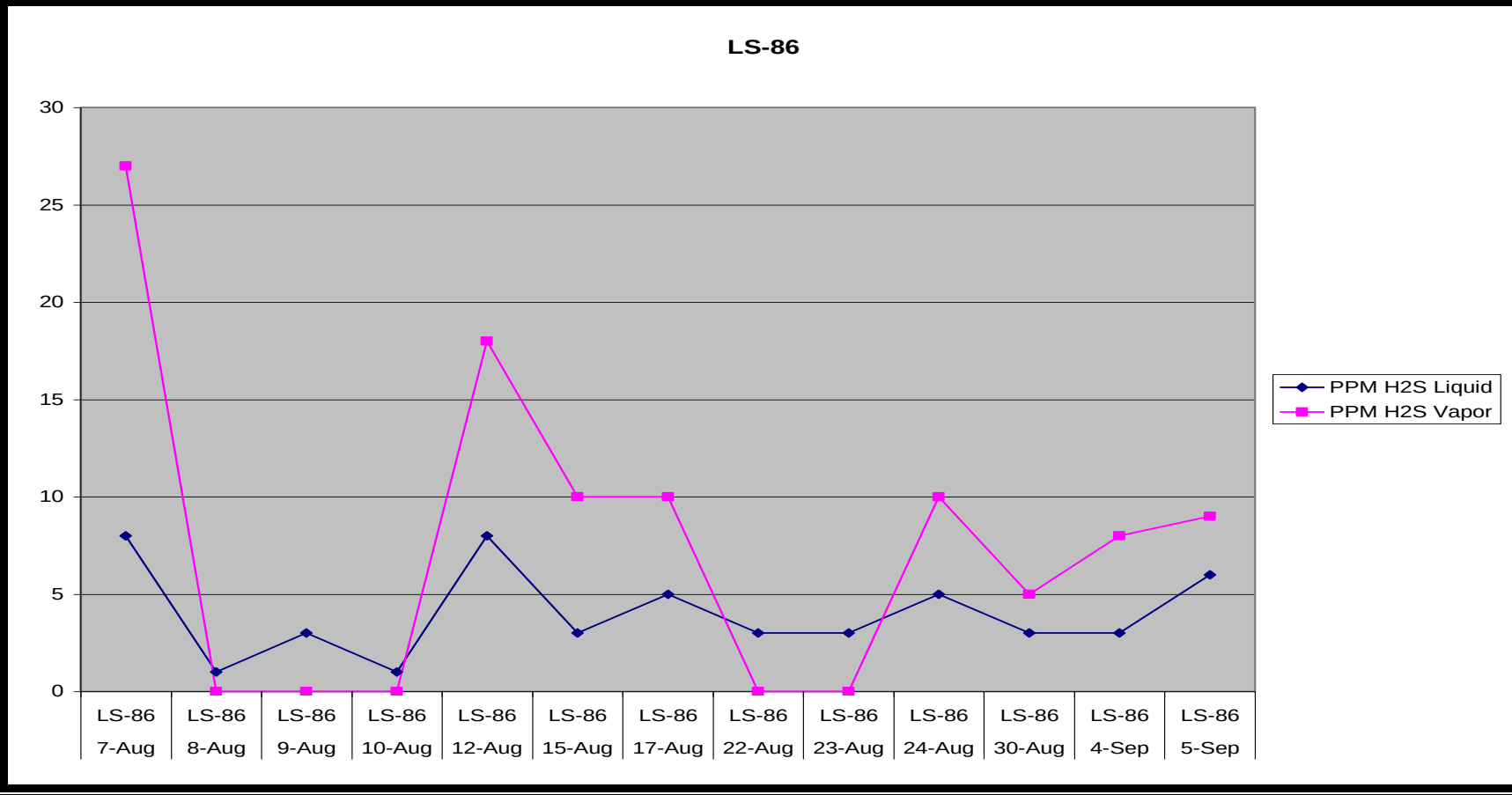
Lift Station 107
During Treatment



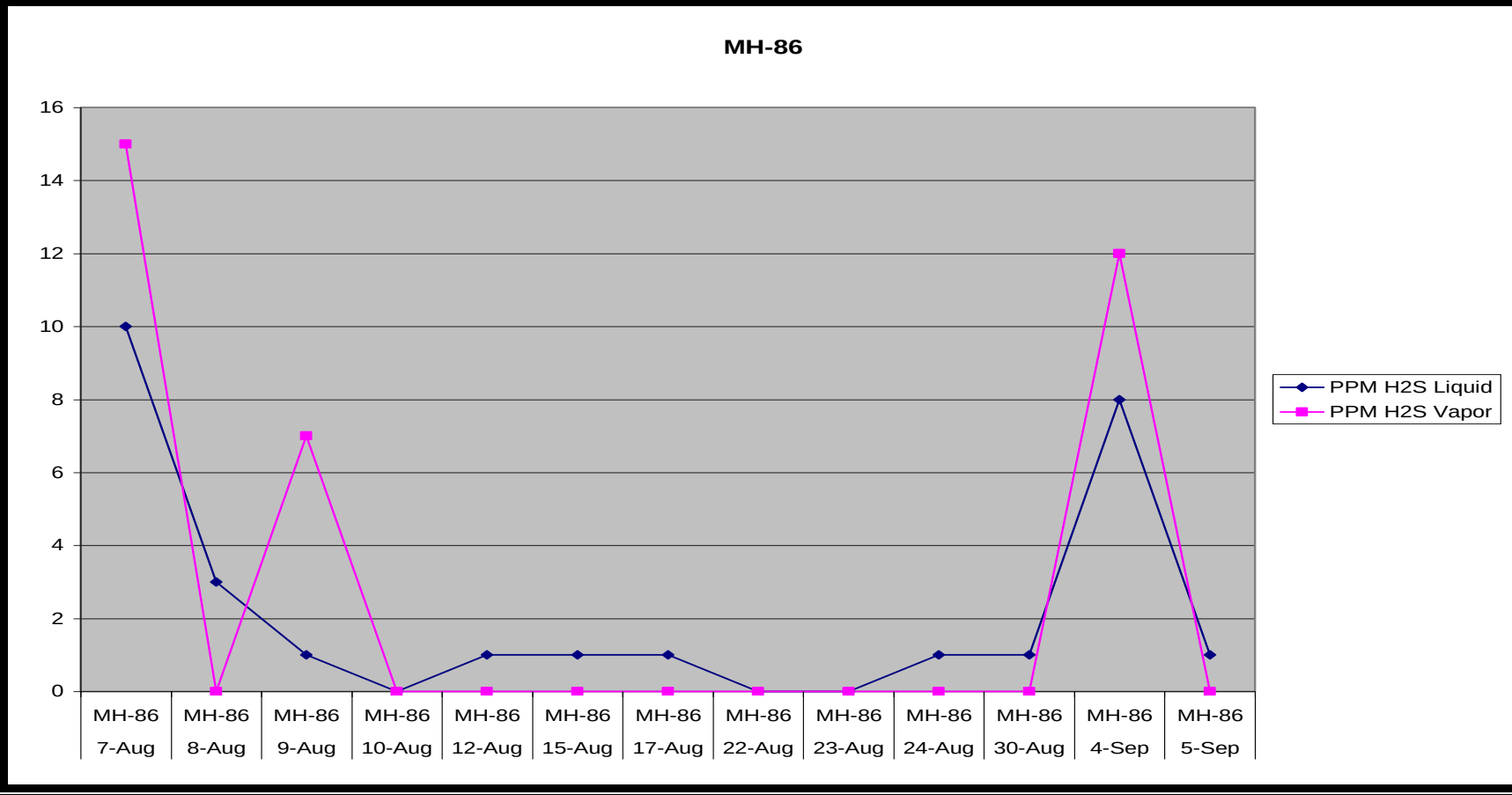
Manhole for LS 107



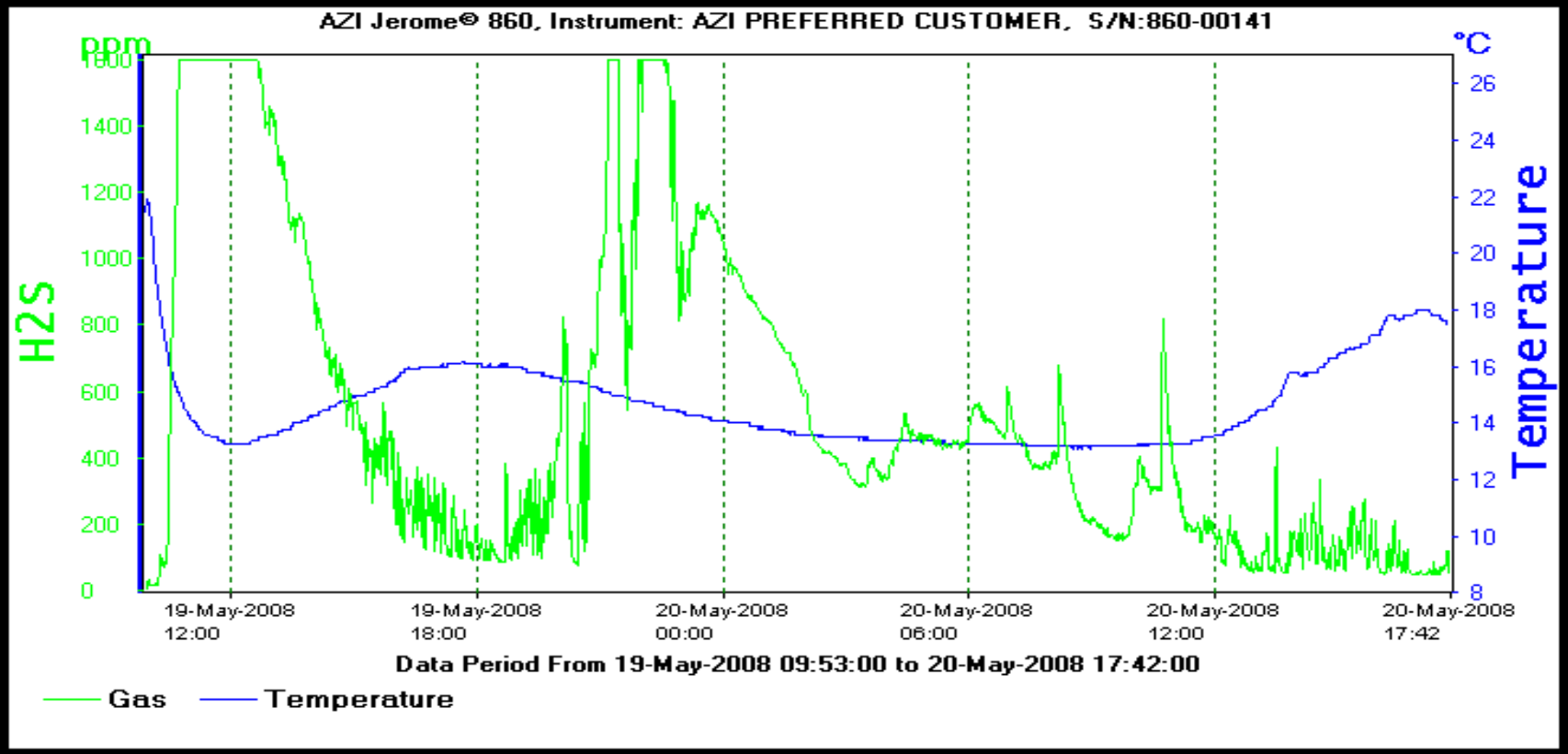
Lift Station 86 with $Mg(OH)_2$



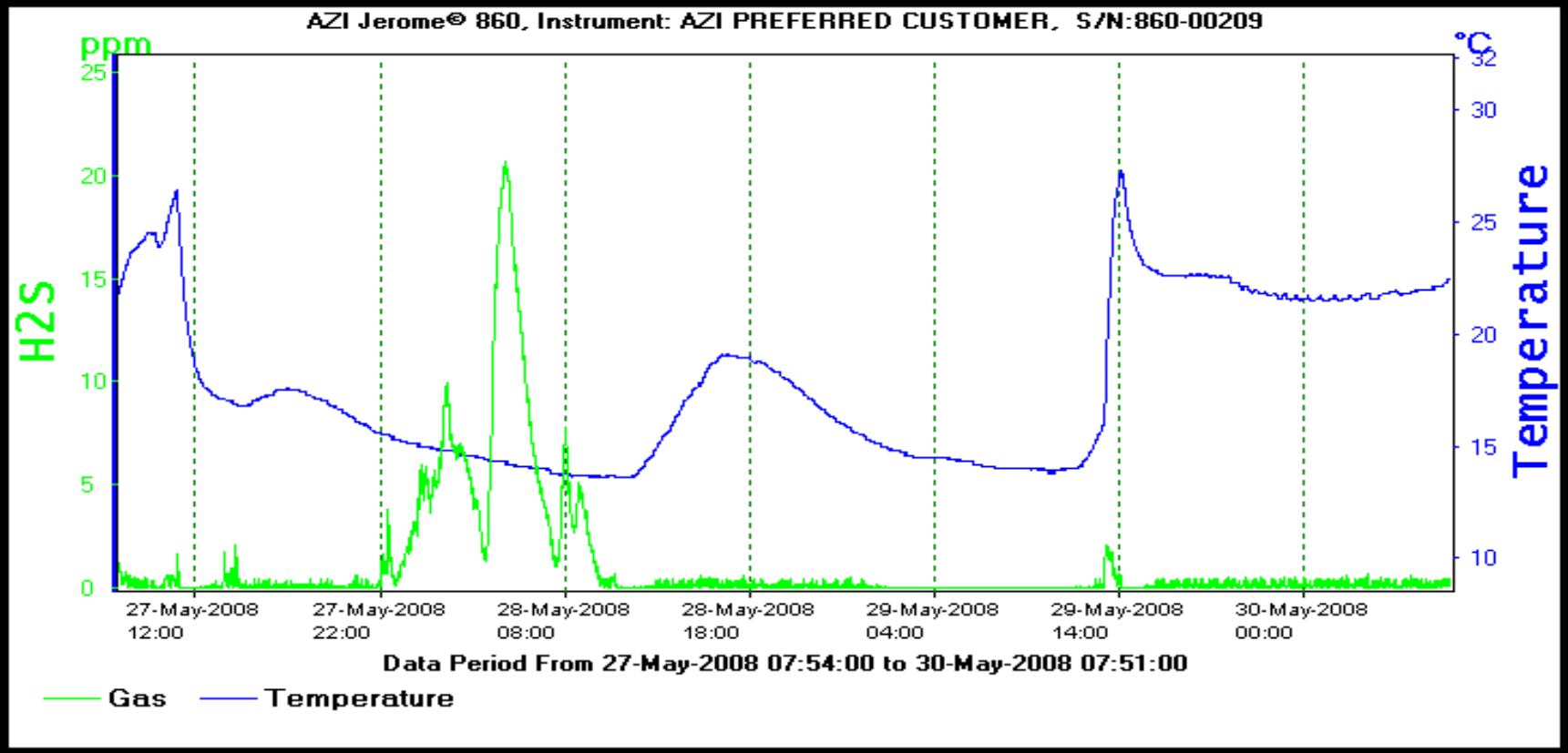
Manhole for LS-86



Case Study # 3 Lift Station 108 Summit County



Lift Station 108 Summit County



Summary using Polymeric Amine Chemistry

- Effective H_2S control
- Reduced maintenance cost
- Reduced solids
- Better odor control
- Safe
- Economical
- Increased equipment life
- Improved public relations

Dry Filter for H_2S Removal in Lift Stations and Plant Applications

Sulfa Clear in Wet Scrubbers

Replacement of Caustic & Bleach

Why Use Sulfa-Clear

- Efficient and cost effective way to remove H_2S
- Reacts to form a corrosion inhibitor
- Reduces maintenance costs
  - Eliminates Acidizing, pH & ORP Probe Calibration,
  - And Eliminates Soft Water Systems
- Eliminates sodium build-up
- Environmentally friendly
- Mercaptan removal
- Use of reclaim water for make-up water

Caustic, Why not?

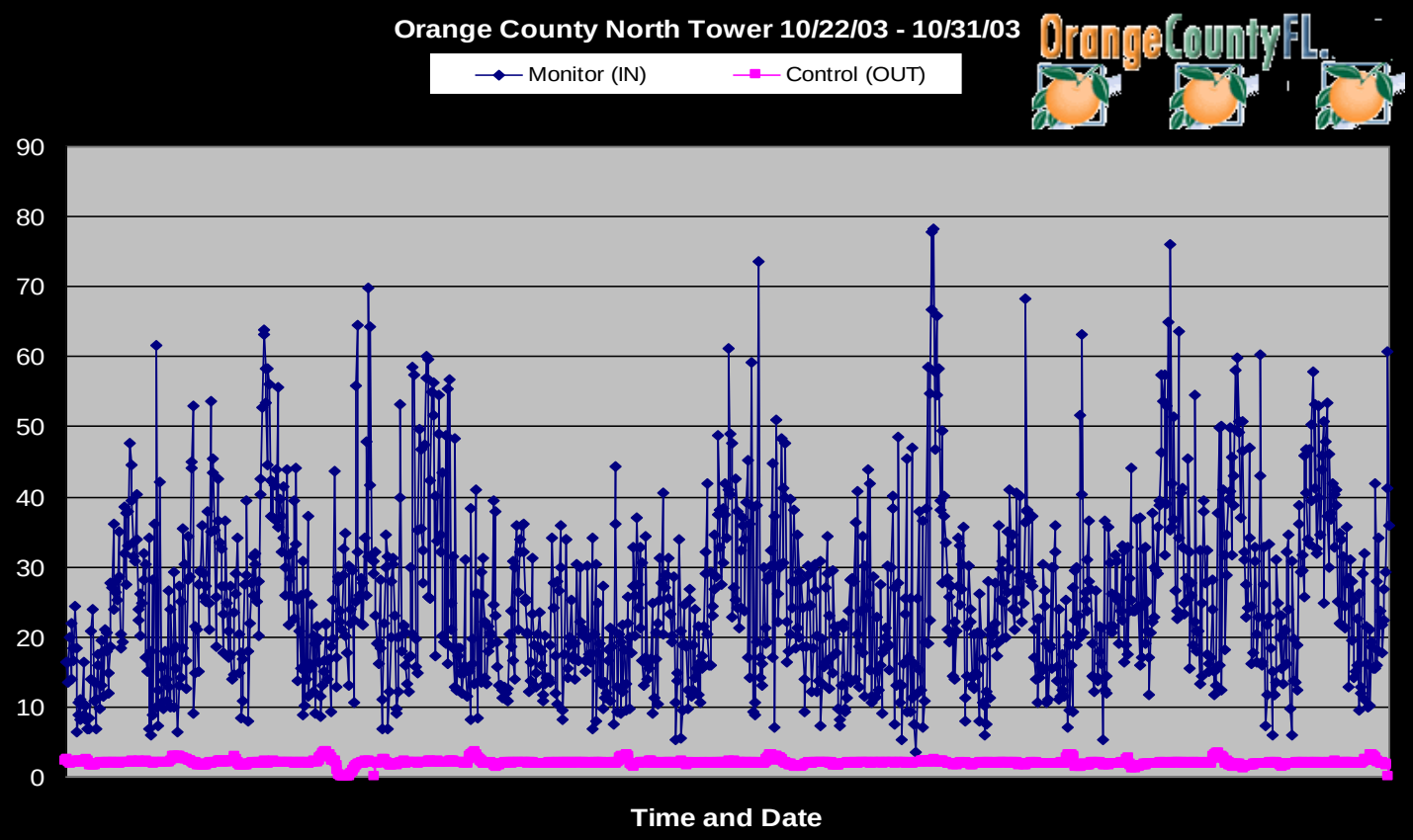
- Highly Corrosive
- Unsafe to Handle
- Hard to store (chemical spills)
- Cleaning of packing material
- Calibration and replacement of pH probes

Caustic Causes Corrosion

Orange County WWTP

Orlando, Florida Sand Lake Facility

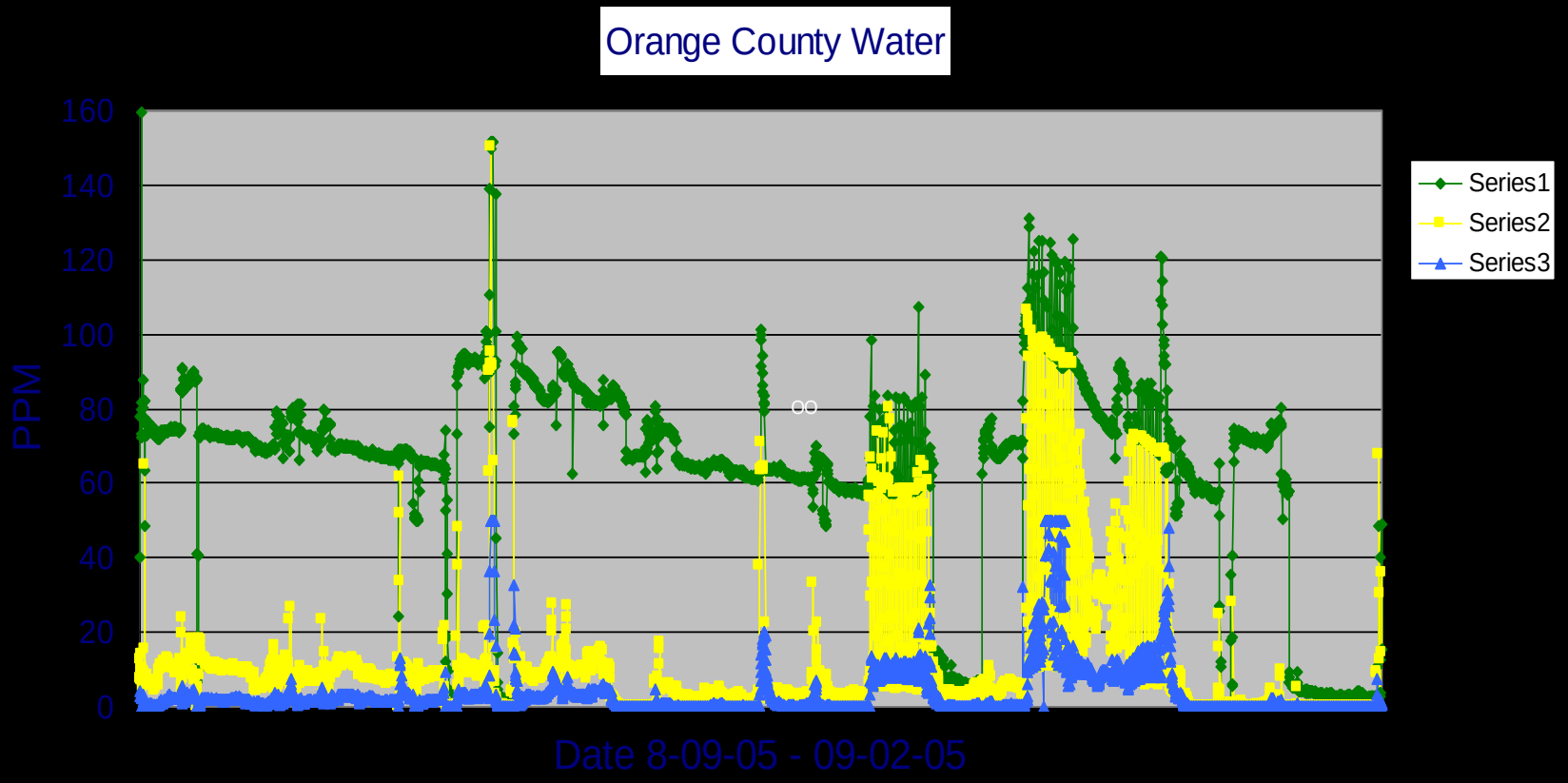
Orange County results using Sulfa-Clear



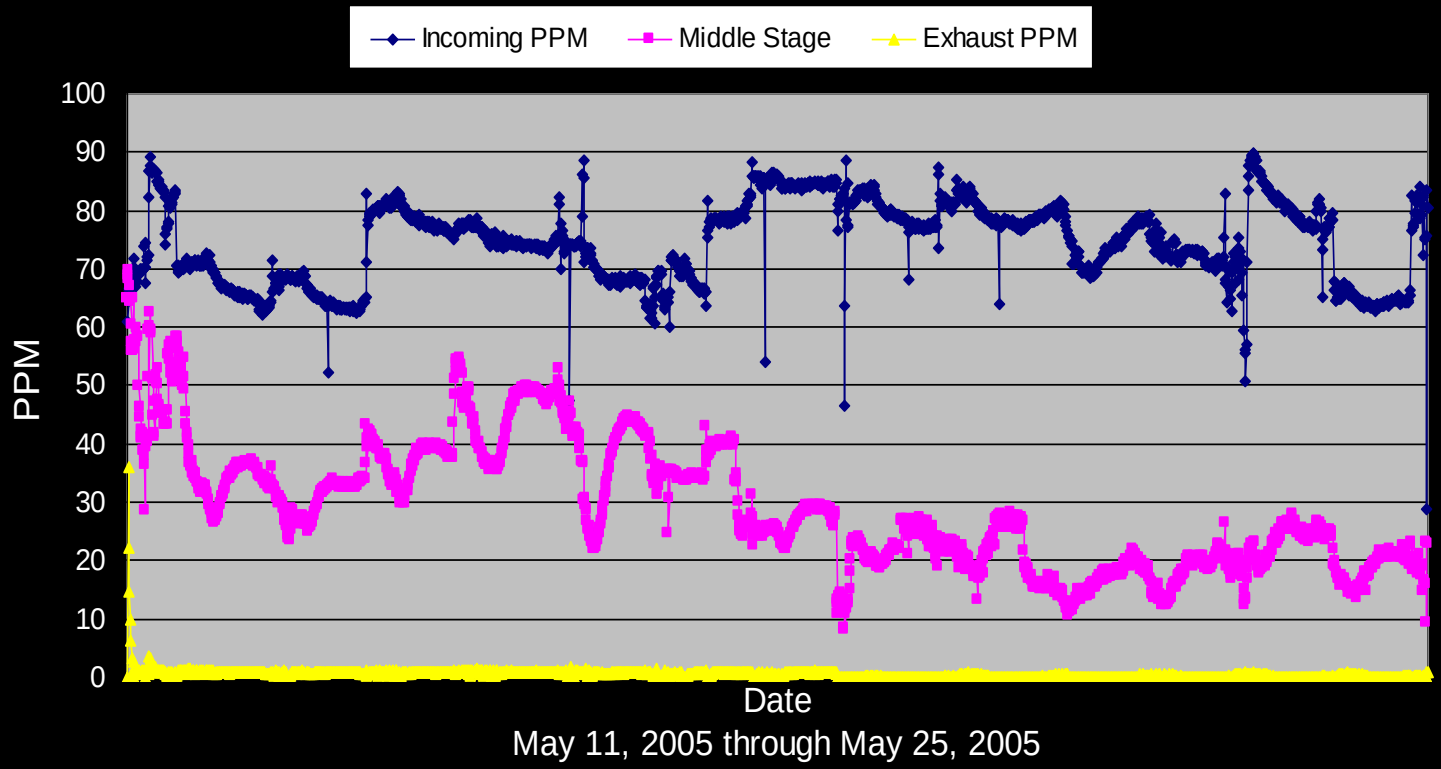
Orange County Water Facility

Curry Ford Road Orlando, Florida

Orange County with Caustic



Orange County with Sulfa-Clear



Summary

- Effective H_2S control
- Reduced plant operating costs
- Reduced maintenance cost
- Reduced sodium build-up
- Better odor control
- Reduced EPA exposure

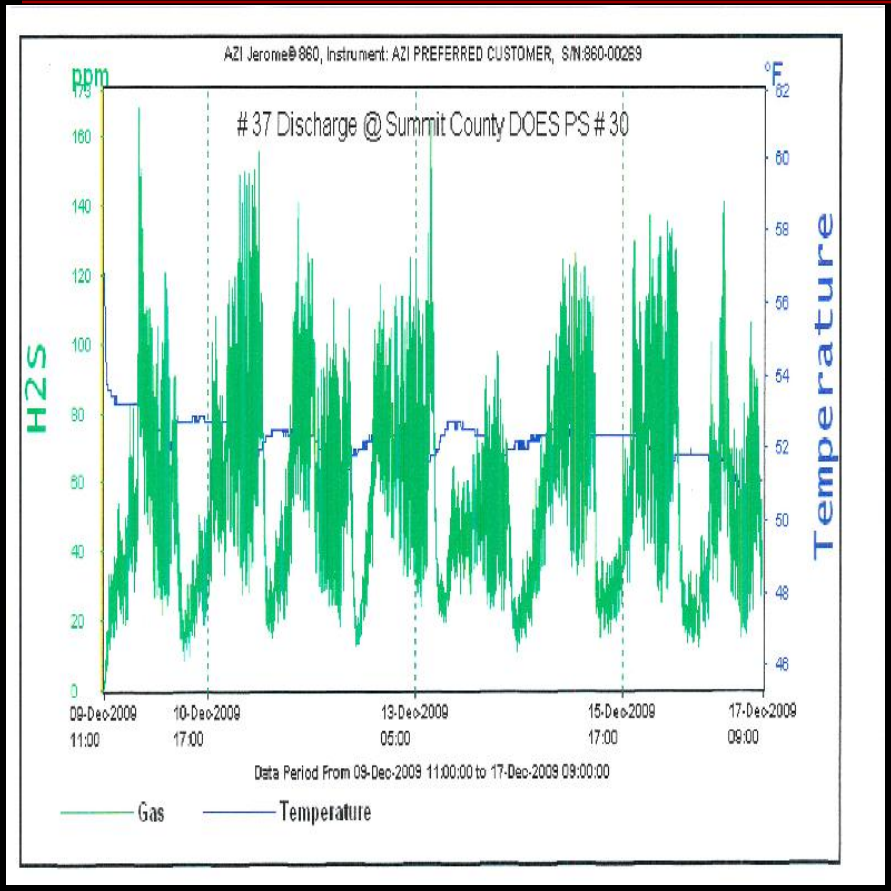
H_2S Removal with a Dry Filter

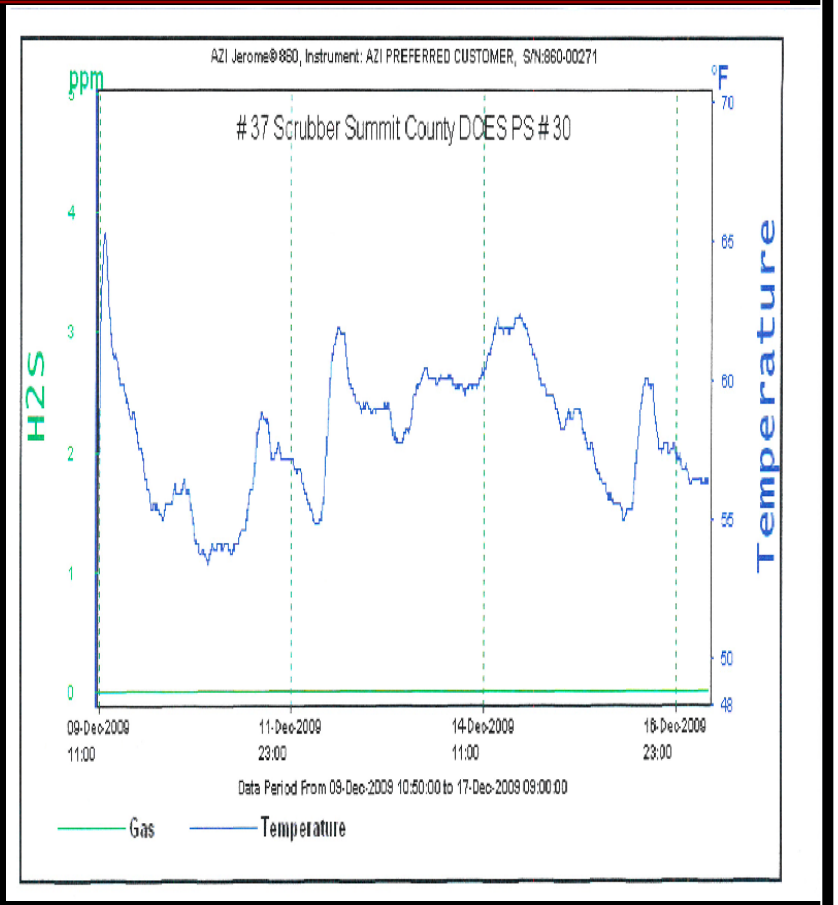
- Lift Station & Plant Applications
- Polymeric Amine Chemistry Impregnated in a Silica Media
- Removes H_2S
- Removes Mercaptan
- Cartridge Design
- Long Lasting Media
- Low Maintenance
- Ease of Disposal

Dry Filter

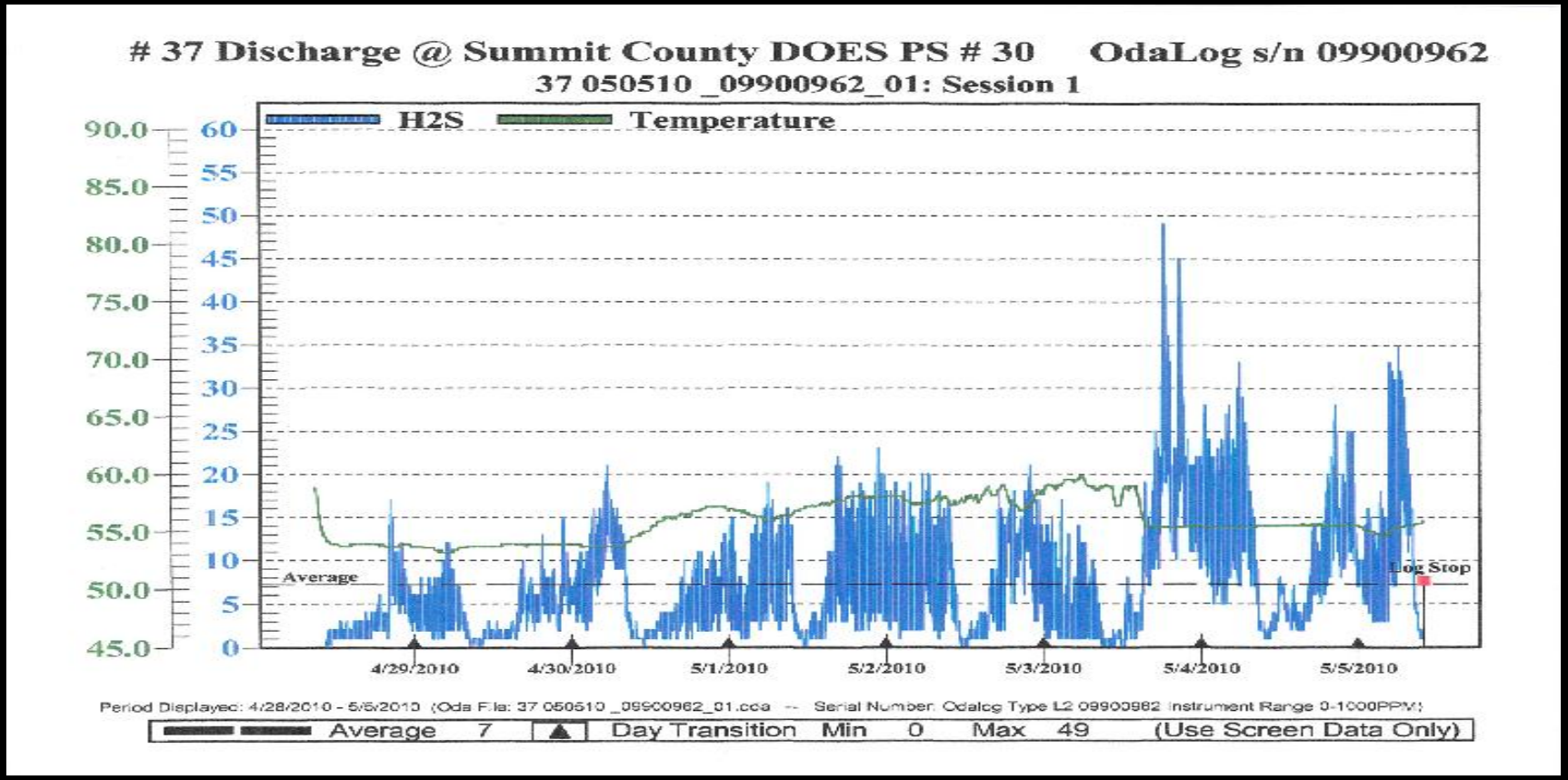
- Readings taken by Odalog & Jerome H_2S logging sensors units
- One placed in the MH or LS
- One in the exhaust of the filter
- Both units are changed weekly
- Media will not solidify

Dry Filter
Initial Data

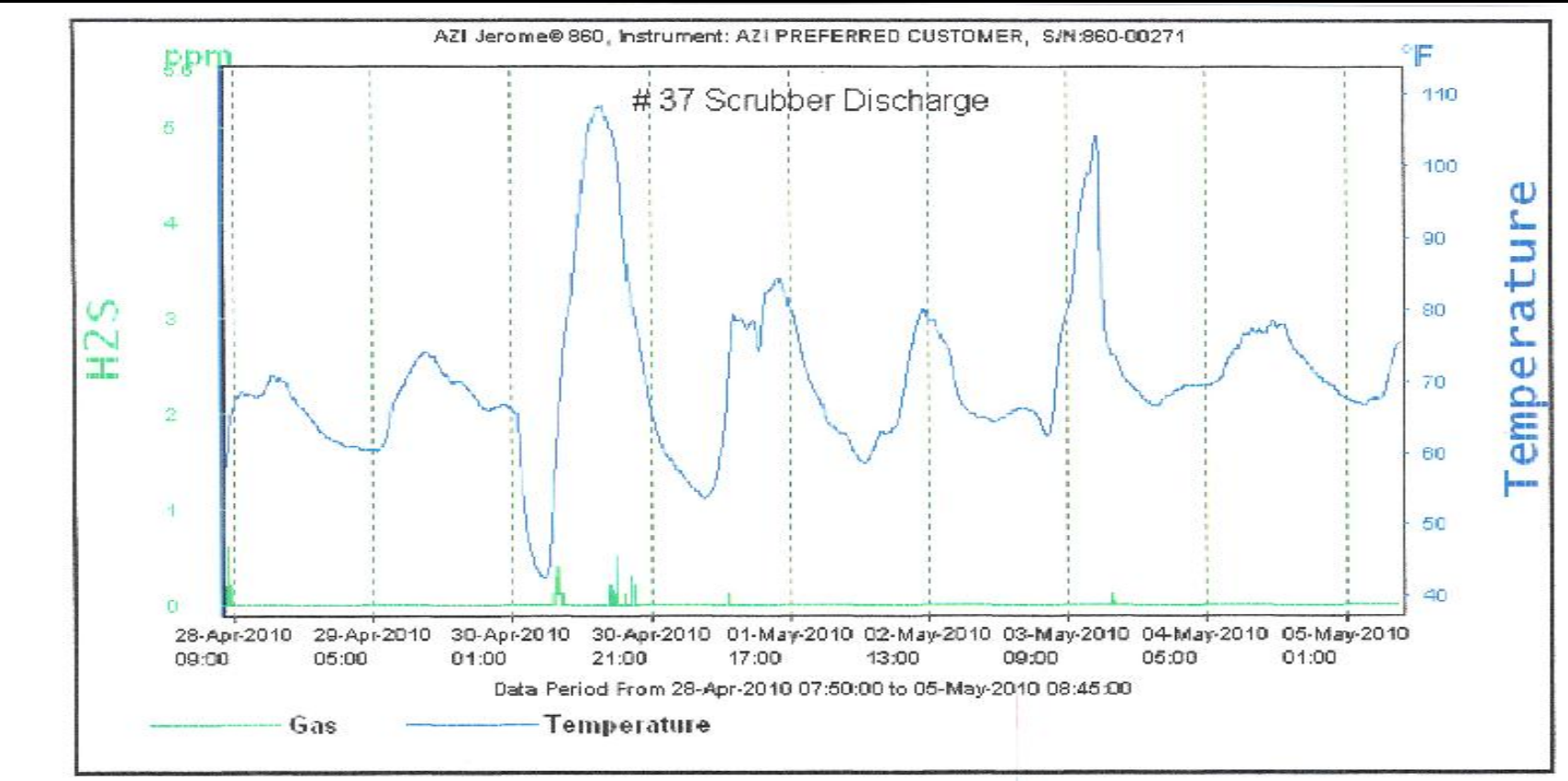




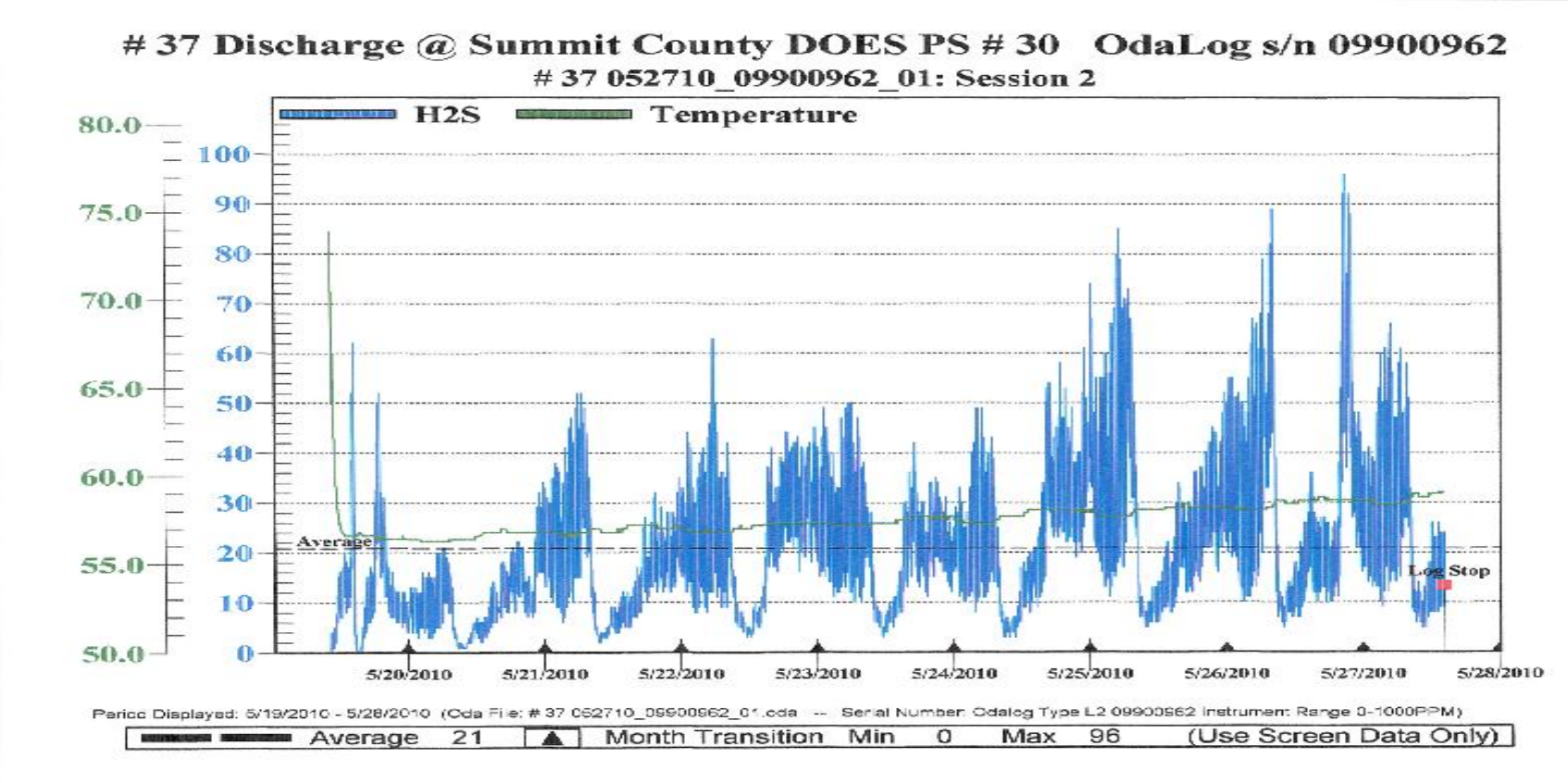
Summit County
Latest Data



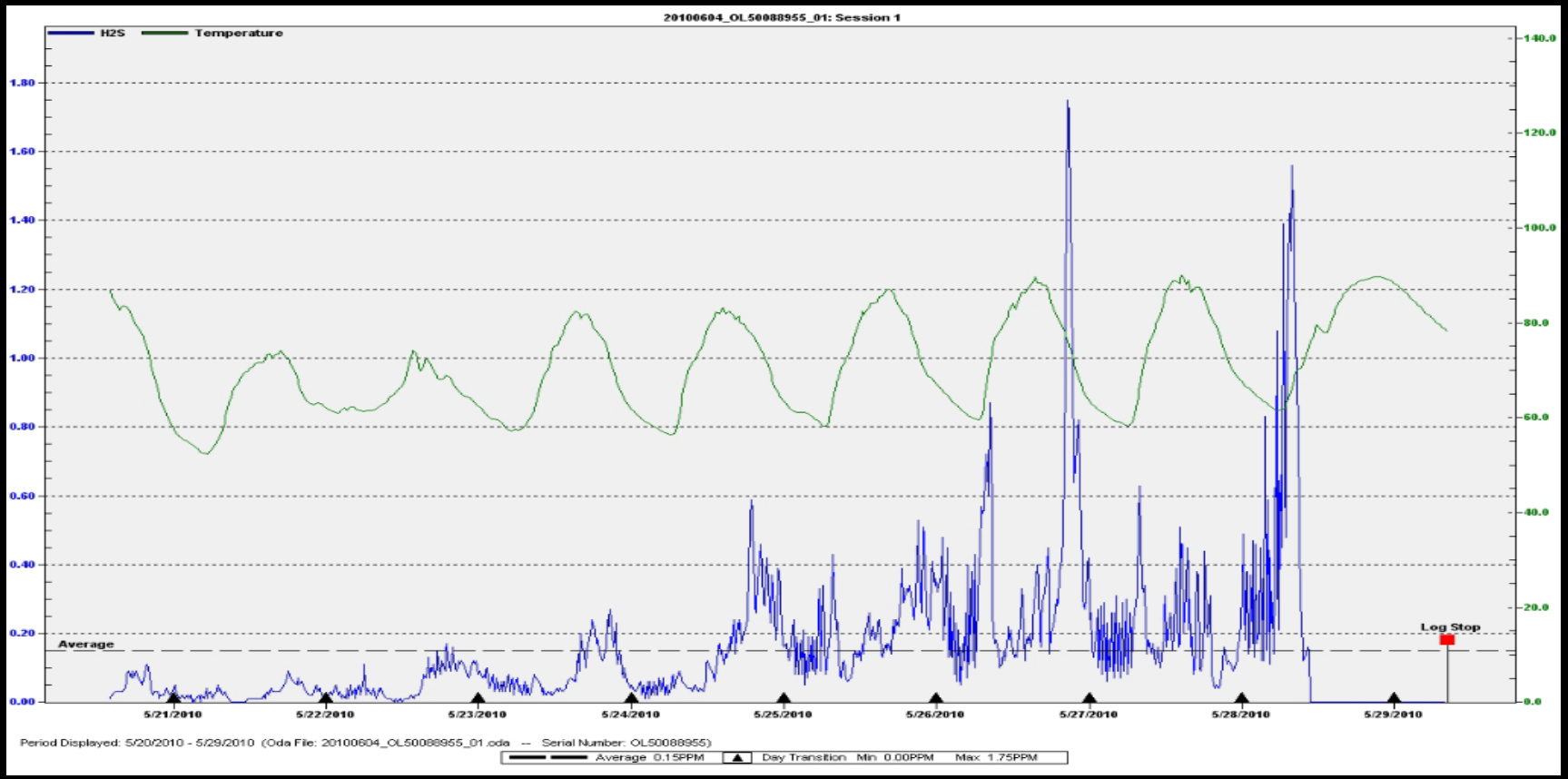
Summit County
Latest Data



Stark County Low Range Input



Stark County Low Range Data



ORM Media

- Silica Media Saturated with Polymeric Amine Chemistry
- Direct Replacement for Activated Carbon
- Direct Replacement for Sulfa Treat Media
- Longer Lasting
- Used in Carbon Canisters
- Used as a Polishing Filter on Bio-Filters

Columbia Analytical Labs

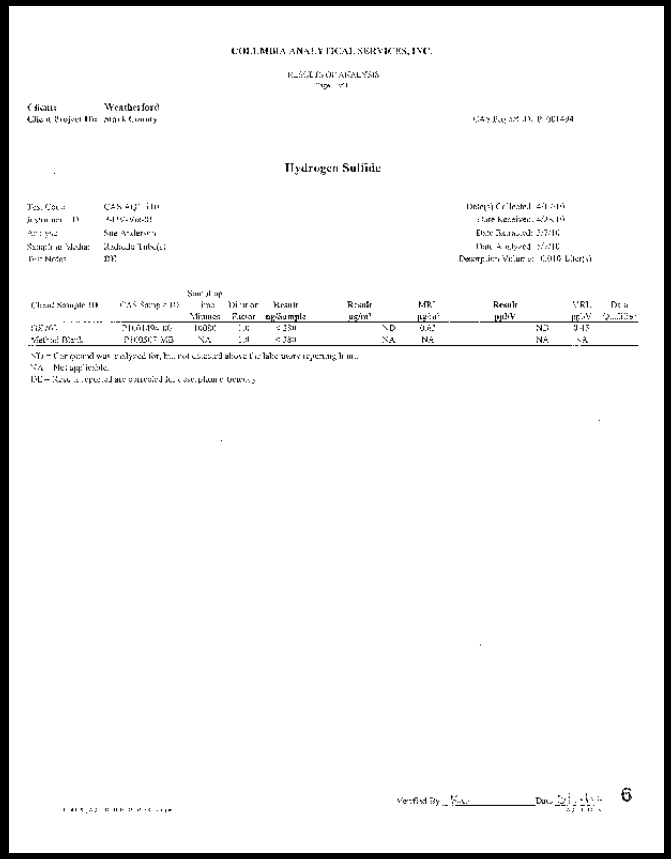
- Measuring results in ppb
- Using Radeillo Samplers
- Less than .05 ppb after five months
- Verifying results using Odalog unit beginning week of 5/17/10

radiello® Sampler

- Passive/diffusive sampling
- Zinc acetate treated
- No holding time issues
- Polyethylene Reporting limit decreases increased duration exposure
  - Potential pptV level sensitivity
- Methylene blue: visible spectrometry

Picture courtesy of Sigma Aldrich

Columbia Results



COLUMBIA ANALYTICAL SERVICES, INC.

RESULTS OF ANALYSIS

Client: Weatherford
Client Project ID: Stark County

Hydrogen Sulfide

Test Code: CAS AQL 1.0
Instrument ID: 8410-Vial-01
Analyst: Sue Anderson
Sampling Media: Radiello Tube(s)
Test Notes: DE

Date(s) Collected: 4/1-5/9
Date Received: 4/5-9/9
Date Extracted: 5/7/10
Date Analyzed: 5/7/10
Desorption Volume: 0.010 Liter(s)

Client Sample ID	CAS Sample ID	Sampling Time Minutes	Dilution Factor	Result ug/Sample	Result ug/m³	MRL µg/m³	Result ppbV	MRL ppbV	Data Qualifier
08365	P100439-06	16080	1.0	< 250	ND	0.62	ND	0.45	
Method Blank	P100507-MB	NA	1.0	< 250	NA	NA	NA	NA	

ND = Compound was analyzed for, but not detected above the laboratory reporting limit.
NA = Not applicable.
DE = Reported value is corrected for desorption efficiency.

Verified By: _____ Date: 5/11/10

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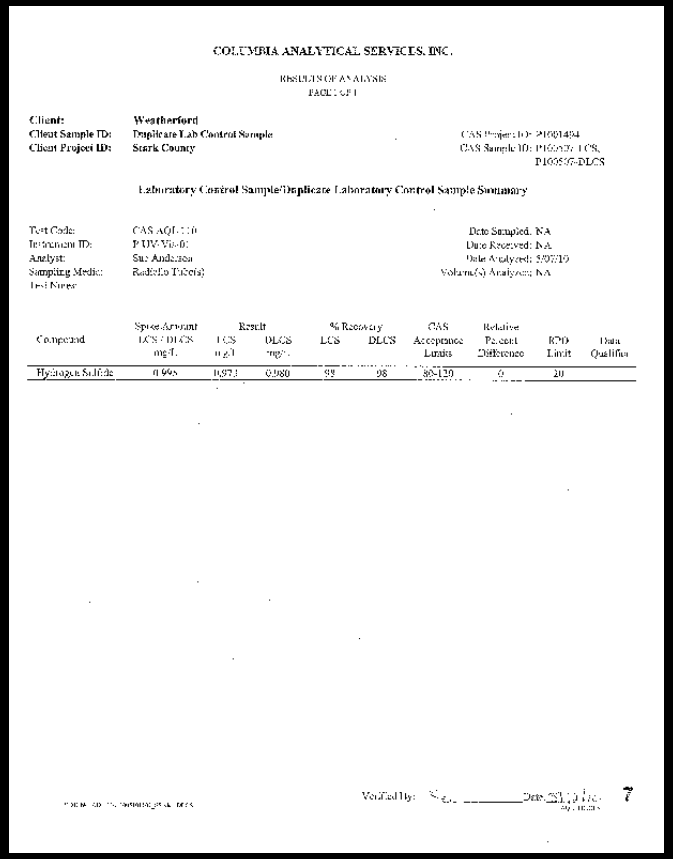

COLUMBIA ANALYTICAL SERVICES, INC.

RESULTS OF ANALYSIS

Client: Weatherford
Client Sample IDs: Duplicate Lab Control Sample
Client Project ID: Stark County

CAS Project ID: P100454
CAS Sample ID: P100507-LCS, P100507-DLCS

Laboratory Control Sample/Duplicate Laboratory Control Sample Summary

Test Code: CAS AQL 1.0
Instrument ID: PUV-Vial-01
Analyst: Sue Anderson
Sampling Media: Radiello Tube(s)
Test Notes:

Date Sampled: NA
Date Received: NA
Date Analyzed: 5/07/10
Volume(s) Analyzed: NA

Compound	Spike Amount LCS / DLCS mg/L	Result LCS ug/l	Result DLCS mg/L	% Recovery LCS	% Recovery DLCS	CAS Acceptance Limits	Relative Percent Difference	RPD Limit	Data Qualifier
Hydrogen Sulfide	0.998	0.973	0.980	98	98	80-120	0	20	

Verified By: _____ Date: 5/11/10

7

Alternatives to Polymeric Amine Chemistry

- Thiogaurd (mag hydroxide)
- Bioxide (calcium nitrate)
- Nitronox (sodium nitrate)
- Potassium Permanganate
- Caustic
- Bleach
- Biological Treatment
- Peroxide (any oxidation)
- Ferrous & Ferric Chloride

Magnesium Hydroxide

- Raises pH keeps pH above 7 and keeps H_2S in a liquid state
- When reaction is spent H_2S will release in vapor down stream
- Very viscous demands constant agitation
- Needs heating in cold weather
- Known to clog pumps and valves

Calcium Nitrate

- Basically calcium nitrate an alternative food source to the SRB bacteria
- When the Calcium Nitrate is consumed the SRB consume sulfates
- Normally the SRB colony has grown needing multiple injection points from the initial start up over a period of time
- Sodium Nitrate causes the same effect as Calcium Nitrate
- However is half the cost of Calcium Nitrate but normally needs twice the consumption rate to achieve the same results
- Calcium Nitrate also forms into what is called a bio-matt that needs to be physically vacuumed from each lift station depending on flow rate or needs constant aeration. It actually looks like a FOG matt

Potassium Permanganate

- It is a true scavenger
- Highly Corrosive
- Precipitates out solids
- Offensive odor

Caustic & Bleach

- Simply pH control
- Raises the pH above 7 forcing H_2S into liquid
- When reaction is spent turbulence will cause H_2S to liberate into vapor
- Very corrosive and hazardous
- Requires special handling

Biological Treatment

- Biofilters and bio-trickling filters work
- To an extent work very well and is the wave of the future
- Normally H_2S returns
- Requires a very large foot print above 80 ppm H_2S
- Normally need a carbon filter to handle break troughs
- Or hopefully the new ORM media to handle breakthroughs better than carbon

Oxidation

- Peroxide or direct air injection
- Adds a third O_2 molecule
- Extra O_2 forces sulfide back to a sulfate stage
- When O_2 is spent SRB bacteria reconsume sulfate and excrete sulfide
- Once again does not remove H_2S

Iron Salts

- Ferrous & Ferric Chloride
- True scavengers
- Precipitate out iron sulfides
- Case studies have shown the precipitants to break pipelines
- Needs agitation
- Not friendly to cold weather

Summary

- Various ways to treat for H_2S removal.
- Each application is different and unique.
- Each application needs evaluation to determine what specific product to use.
- Thank you & Questions.

Wake Up It is Over

- Questions?