

Improving Sour Water Injection using Synergy Services FeS-X Products

Presented at

2010 PRODUCED WATER SOCIETY 20th ANNUAL SEMINAR

January 20 – 22, 2010

Author

Johnny D Richard

Shell Exploration and Production Company

Contributors:

Mark Maddox, President/CEO Synergy Services Inc

Ben Smith, Synergy Services Inc

Keith Jackson, Synergy Services Inc

Rob “Bob” Long, Synergy Services Inc

Abstract:

Re-injection of produced water has historically offered as much or a greater challenge to manage as compared to disposal of produced water overboard in the Gulf of Mexico. In an area like Mobile Bay Alabama, zero discharge is the regulation; therefore all water must be disposed of at an onshore location. Since the typical produced water in this area is sour, there can be a broad range of particulates in the water. The matrix of the water can be scales (calcite, barite, and sulfides), salt, clays and the ever-present hydrocarbons. During the process of finding a solution to the plugging of exchangers in the gas treating plant, we noticed with chemical injection the improved performance of the disposal well. This presentation briefly covers the experience of the application of Synergy Services FeS-X products that improved the performance of the well.

Introduction

As the title of the presentation suggest, the primary topic focus is centered on improving the injection performance of the Plant disposal well. In reality in our sour gas plant, the main problem was the excessive plugging of the sour water heat exchangers used to pre-heat the water for dissolved hydrogen sulfide removal and cool the water prior to disposal. Iron sulfide being the sticky nuisance that it is was also creating separation issues for the primary separator feeding the exchangers and finally binding all the contaminants at the bottom of the disposal well. Upstream of the disposal well water was coming from other sources in the gas plant that may be sour or sweet (no measurable H₂S) that was intermittently pumped to the waste water storage. These sources if improperly treated or even with the proper chemical inhibition also add to the problem.

Project Problem Description:

- 1) Sour gas plant experiencing plugging issues in the exchangers of the Sour Water Stripper System
- 2) Onsite disposal well injection pressure is at state regulated 1550 psi @ 150 gpm disposal rate
- 3) Performance of primary separator (3 phase) for sour water handling decreases during maintenance pigging operations

Solution:

- 1) Determine if chemical treatment can be used to address the major problem

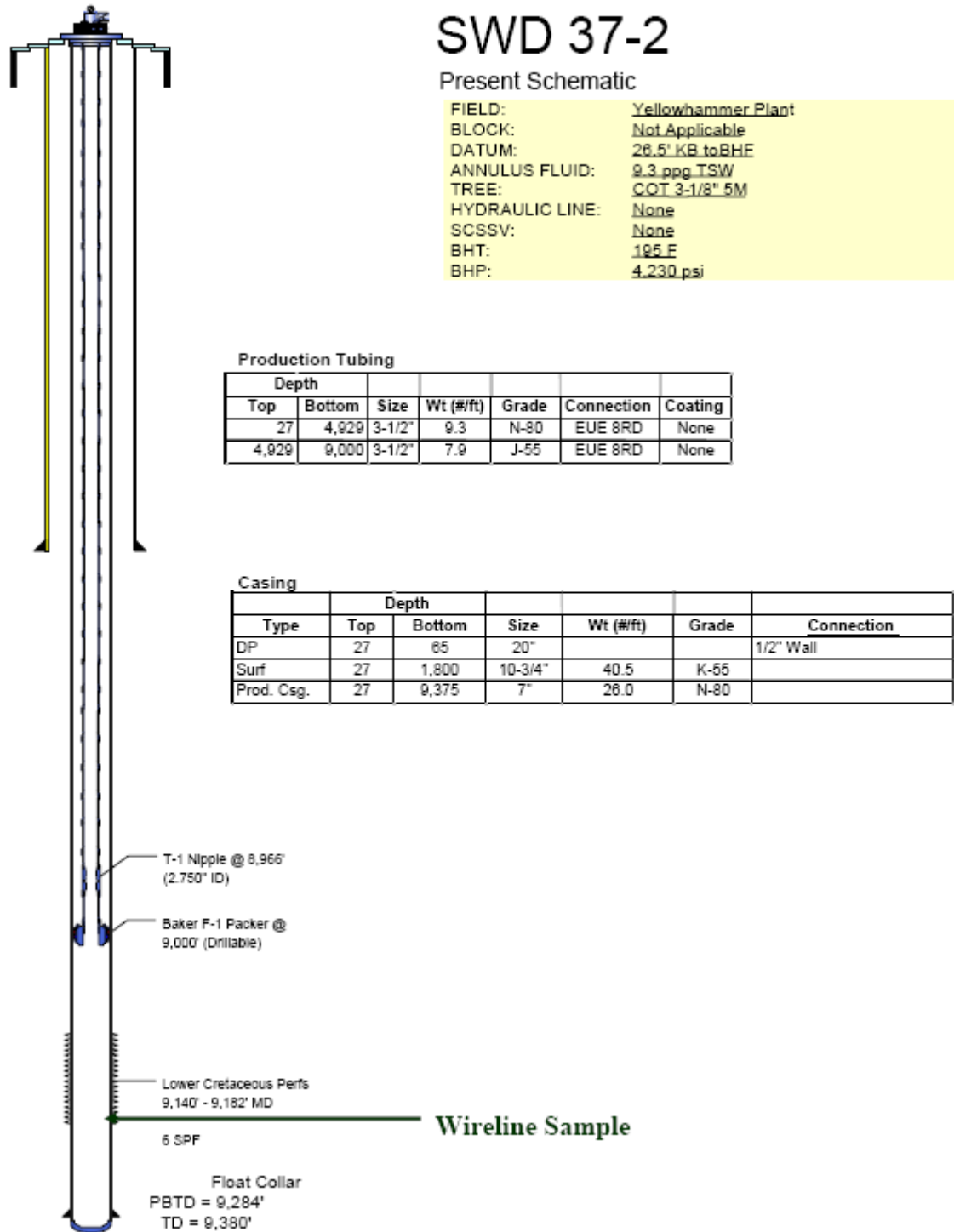
Results: Chemical treatment resulted in improving some areas in the system but a better solution is a solids management system with chemical treatment.

Methodology:

I. Disposal Well Review

Figure 1: Well Schematic

Attachment 1 (Current Mechanical Schematic)



As can be seen in Figure 1 of the well sketch, the existence of what is primarily called a “Rat Hole” at the bottom of the well which allows for loose debris and sometimes lost wireline tools.

A deposit sample was collected from this location and the wireline survey did not reveal any obstructions covering the perforations. The analyses of the deposit can be seen in figure 2, figure 3 and figure 4.

Figure 2: FTIR

I. FTIR Analysis

The material was dried to remove water and then extracted for FTIR analysis. The material was found to be approximately 90% solids.

Infrared Spectroscopy (FTIR) per ASTM E1252-98 (07) and ASTM E334-01 (07)

Test	Description/Prep Method	FT-IR Spectrum	Results/Characteristics
1	Hexane soluble component	Figure 1	Mixture, aliphatic and aromatic hydrocarbons
2	Water soluble component	Figure 2	Ether type glycol

Figure 3: XRD

X-Ray Diffraction Mineralogical Analysis⁵¹

Mineral Constituents	Chemical Formula	Relative Abundance (%)
Quartz	SiO ₂	49
Plagioclase Feldspar	(Na,Ca)AlSi ₃ O ₈	2
K-Feldspar	KAlSi ₃ O ₈	1
Calcite	CaCO ₃	12
Halite	NaCl	1
Barite	BaSO ₄	24
Iron	Alpha-Fe	2
Austentite	Fe-C	7
Clay/Mica	--	2
	Total	100

Figure 4: EDXA

Energy Dispersive X-ray Analysis Results⁵¹

Parameter	Concentration (Wt. %)
Aluminum	3.00
Silicon	47.33
Sulfur	14.44
Chlorine	1.04
Potassium	1.16
Calcium	9.96
Iron	9.35
Barium	13.72
Total	100.0

General interpretation of the composition is a majority of sand, barite, calcite bounded by iron sulfide and hydrocarbons. It is probably not a good assumption to anticipate the percentage of plugging in due mostly to sand based on this analysis. What we have to keep in mind is that the “Rat Hole” collects the items that are less suspended in the water and that would have a tendency to fall out if given an opportunity.

In the figure 5, figure 6 and figure 7, we can see the composition of the water.

Figure 5: Cations

YH SWD #2 Input Profile

Cations	Offshore 17 miles away		Prior to Sep	1600 BWPD	??BBLs	SWD #2 9/12/08	
	Fairway		YH				
	34244-01 7/26/2008 23:30:00 (mg/l)	34244-02 7/28/2008 03:00:00 (mg/l)	Upstream of V100 Sep 9/12/2008	Produced Water Stripper 9/12/08	Process Sour Water Stripper 9/12/08		
Barium	535	520	630	715	0.03	500	
Cadmium	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	
Calcium	19,100	18,730	21,420	24,480	1.2	20,600	
Chromium	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	
Cobalt	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Copper	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	
Iron (dissolved)	<0.01	<0.01	5.4	10	<0.01	13	
Iron (total)	<0.01	<0.01	28	11	<0.01	17	
Lead	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	
Lithium	31	30	45	50	<0.005	31	
Magnesium	580	570	745	875	0.06	605	
Manganese	155	155	190	220	<0.002	155	
Molybdenum	<0.044	<0.044	<0.044	<0.044	<0.044	<0.044	
Nickel	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	
Phosphorus	<0.17	<0.17	<0.17	<0.17	<0.17	2.0	
Potassium	5,100	5,010	6,170	7,140	<0.17	4,620	
Silicon	34	35	60	50	1.0	52	
Sodium	43,590	42,600	49,620	57,240	1.3	44,050	
Strontium	920	900	960	1,110	<0.16	775	
Vanadium	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Zinc	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	

Figure 6: Anions

Anions	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
Bicarbonate	31	145	34	49	2,140	270
Borate	150	145	205	195	<0.004	155
Bromide	650	645	780	880	<1.0	625
Carbonate	0	0	0	0	0	0
Chloride	106,430	104,570	128,570	147,630	59	103,010
Fluoride	<1.0	22	28	17	<1.0	30
Iodide	<2.0	140	<2.0	<2.0	<2.0	<2.0
Nitrate	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Nitrite	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Phosphate	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sulfate	<1.0	<1.0	18	<1.0	<1.0	<1.0
Sulfide	0	0	0	0	0	0

Figure 7: Organic Acids

Organic Acids	(mg/l)	(mg/l)					
Acetate	12	14					
Butyrate	0	0					
Formate	0	0					
Glycolate	0	0					
Propionate	0	0					
Valerate	0	0					
pH	5.73	6.00	4.40	4.78	7.26	5.98	
S.G.	1.1235	1.1205	1.1472	1.1672	1.0014	1.1159	

As you might observe, there is the potential for a lot of things to occur in relation to scale. Like most analysis it does not always tell the whole story. Lead and zinc are not shown but when you start removing scale from wells, flowlines, pipelines and facility piping, they are usually in the mixture. What is unique about iron sulfide in the mix is its ability to latch on to every particle to either bind it to the wall of the pipe, or increase the buoyancy of the particle to create floaters suspended in the water. Knowing this can be an advantage in certain parts of the system but a disadvantage in others.

Figure 7A: Water Analyses 2009 suggest that with the improved scale squeeze program, that is squeezing the 2 out of the three biggest water makers, we have a lot more dissolved elements in the water. Unfortunately looking at the Ba numbers we might not have enough inhibitor to prevent deposition in the pipeline. The manganese numbers are misleading and are normally used in sweet systems to monitor for active corrosion of carbon steel pipe. It was included in the original monitoring specification but new findings suggest that this technique needs to be revisited in sour systems.

Complete Water Analysis with Common Metals					
	19-May-09	19-May-09	12-May-09	12-May-09	12-May-09
Cations	8" PL Fairway	8" PL Plant	V-100	E-103	T-703
Barium	1,010	645	630	640	465
Calcium	29,970	21,240	20,860	21,390	17,210
Copper	<0.009	<0.009	<0.009	<0.009	<0.009
Iron (dissolved)	55.0	37	41	44	<0.01
Iron (total)	55.0	37	43	44	<0.01
Lead	<2.2	<2.2	<2.2	<2.2	<2.2
Magnesium	970	760	730	735	540
Manganese	255.0	190	190	195	130
Nickel	<0.02	<0.02	<0.02	<0.02	0
Potassium	10,210	5,420	6,380	6,520	4,710
Silicon	75.0	61	54	54	24
Sodium	70,190	46,360	50,270	51,230	39,420
Strontium	1,240	955	915	945	660
Vanadium	<0.01	<0.01	<0.01	<0.01	<0.01
Zinc	1.4	<0.004	<0.004	<0.004	<0.004
Anions					
Alkalinity (as Bicarbonate)	59	51	82	78	695
Borate	260	<0.004	200	205	150
Bromide	1,060	700	760	775	585
Carbonate	0.0	0.0	0.0	0.0	0.0
Chloride	172,600	119,660	118,150	121,660	91,570
Iodide	<2.0	<2.0	<2.0	<2.0	<2.0
Sulfate	<1.0	<1.0	16	15	9
Sulfide	0.0	0.0	0.0	0.0	0.0
pH	7.18	4.60	4.88	4.99	7.26
SG	1.1902	1.1380	1.1379	1.1420	1.1071

Figure 8 shows what can be described best as a typical but not always the case a visual description of the outlet of water of vessels in the sour water system.

Figure 8: V-100 (Produced Water De-emulsifier), E-103 (Shell side) Sour Water Heat Exchangers and the T-703 (Wastewater Storage Tank) which is immediately upstream of the disposal water pump prior to the well.



Oil in water in itself is not a major issue for disposal wells until the oil is contaminated with suspended solids. Figure 9 shows the Wastewater storage tank and the guard filter for the disposal pump and the O&G analysis is shown in Figure 10.

Figure 9:

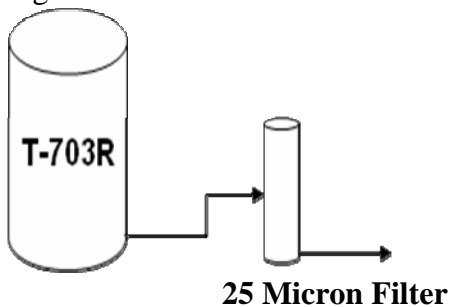


Figure 10: EPA 1664 HEM & SGT HEM

SWD 37-2 O&G				
Client Sample ID	Collection Date	Analyte	Result	Unit
T-703R Outlet	10/8/2009 13:45	HEM (Oil & Grease)	600	mg/L
T-703R Outlet	10/8/2009 13:45	Silica Gel Treated n-Hexane Extractable Material	400	mg/L
T-703R Outlet	10/9/2009 7:13	HEM (Oil & Grease)	750	mg/L
T-703R Outlet	10/9/2009 7:13	Silica Gel Treated n-Hexane Extractable Material	500	mg/L
T-703R Filter Outlet	10/9/2009 8:00	HEM (Oil & Grease)	900	mg/L
T-703R Filter Outlet	10/9/2009 8:00	Silica Gel Treated n-Hexane Extractable Material	630	mg/L
Date	Sample ID	TOG	TPH	WSO
10/8/2009 13:45	T-703R Outlet	600	400	200
10/9/2009 7:13	T-703R Outlet	750	500	250
10/9/2009 8:00	T-703R Filter Outlet	900	630	270
TOG:	Total Oil & Grease which is Total Petroleum Hydrocarbons + Water Soluble Organics			
TPH:	Total Petroleum Hydrocarbons mostly refers to dispersed oil droplets in the water			
WSO:	Water Soluble Organics is soluble oil or weak acids or sub micron oil droplets in the water			

Of course installing a better filtration system that would allow oil skimming from the top of the filter pot is one of the goals to improving the well performance but is not specifically covered in this presentation. To the defense of the original design philosophy, all the vessels with the exception of the new filter pot, the O&G content from the V-100 has been as low as 10 PPM TOG. That would definitely be acceptable and a target to shoot for continuously for future improvements.

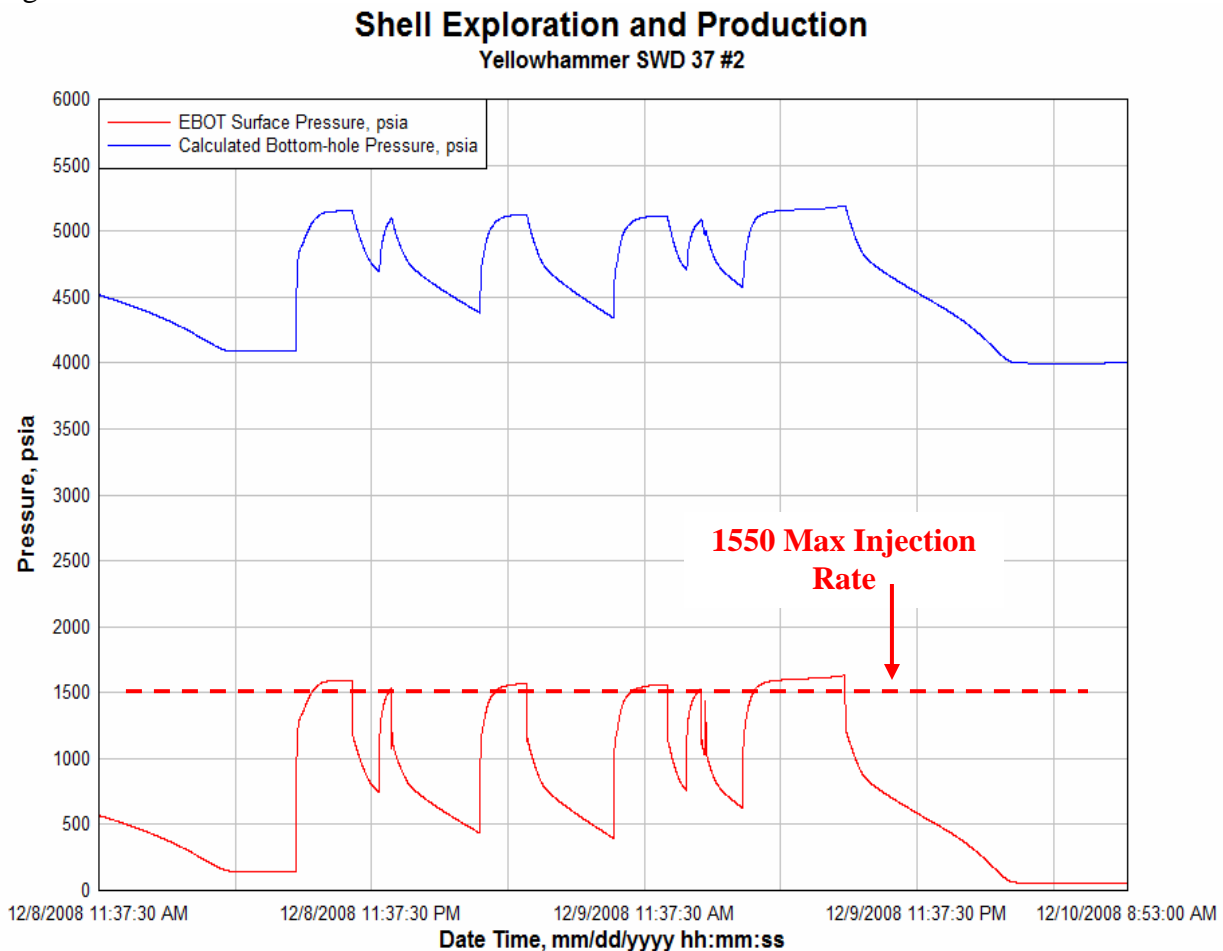
II. Injection Well Testing

The next question to be answered prior to either finding another disposal zone or re-perforate the well was to do an injection well test with a well services company. This would determine how the well would respond at a constant pressure and rate. Results of this test are shown Figure 11.

Figure 11:

Max. Allowable THP	1550	psi
Frac Gradient	0.673	psi/ft
Fluid Gradient	0.465	psi/ft
Injection Depth	9160	ft
Max. BHP	5809.4	psi
Frac Pressure	6164.68	psi
Margin to Frac	355.28	psi

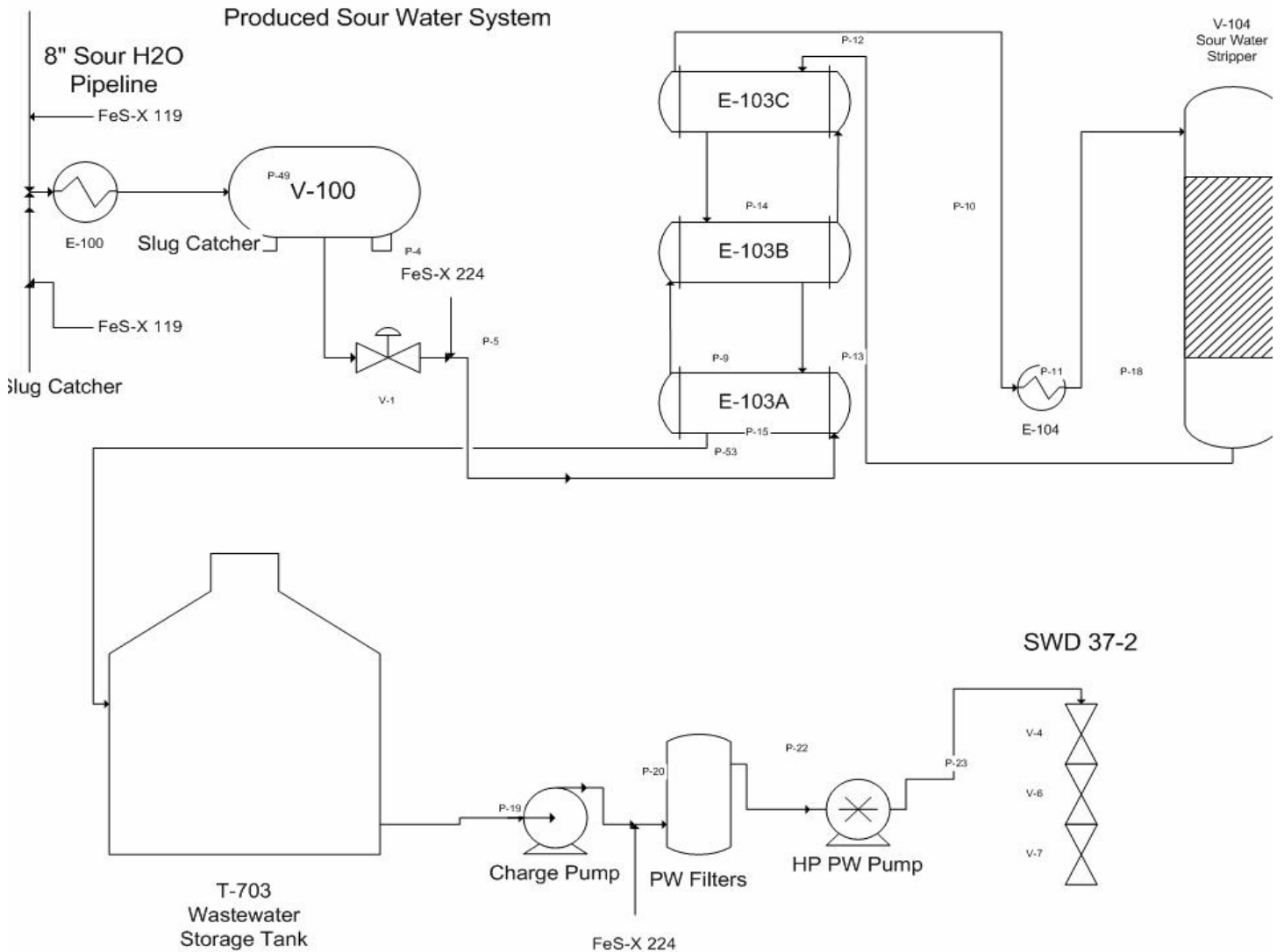
Figure 11a:



Based on the results in Figure 11a, leads us to believe there is plugging as seen by the increasing pressure topsides and at bottom hole conditions. All plans were to try some Well Flow barite dissolver products to not only remove the potential calcite scale but also the more difficult barite scale. Prior to initiating the program, we starting seeing the well improve after beginning the

FeS-X chemical injection at the front end of the sour water system. Figure 12 below shows the simplified sour water stripping process.

Figure 12: Sour Water Stripper System with FeS-X chemical injection points



Typical Flow:

- 1200 – 1600 BWPD (Barrels of Water per Day)
- Weekly Disc Pig in 8" Pipeline
- <1 feet/sec fluid velocity in 8" Pipeline
- Corrosion inhibitor batch every 3 weeks with Brush Pig in front
- Slug Catcher fluid: Condensed water and corrosion inhibitor batches from 12" & 16" Gas gathering lines. Fluid processed at the now recommended rate of 5 gpm.
- Open Drain Sump pump discharges upstream of T-703 wastewater tank (not shown). This particular pump when in service discharges at a rate of 150 gpm, which of course

exceeds the capacity of the disposal well pump. However the fluid volume is mostly small and is usually not a major issue unless during heavy rains. You guess it; we had heavy rains in 2009.

III. Solids Distribution:

Figure 13 below gives a view of the particle size distribution in the water leaving the production platform 17 miles away and at the inlet to the gas plant.

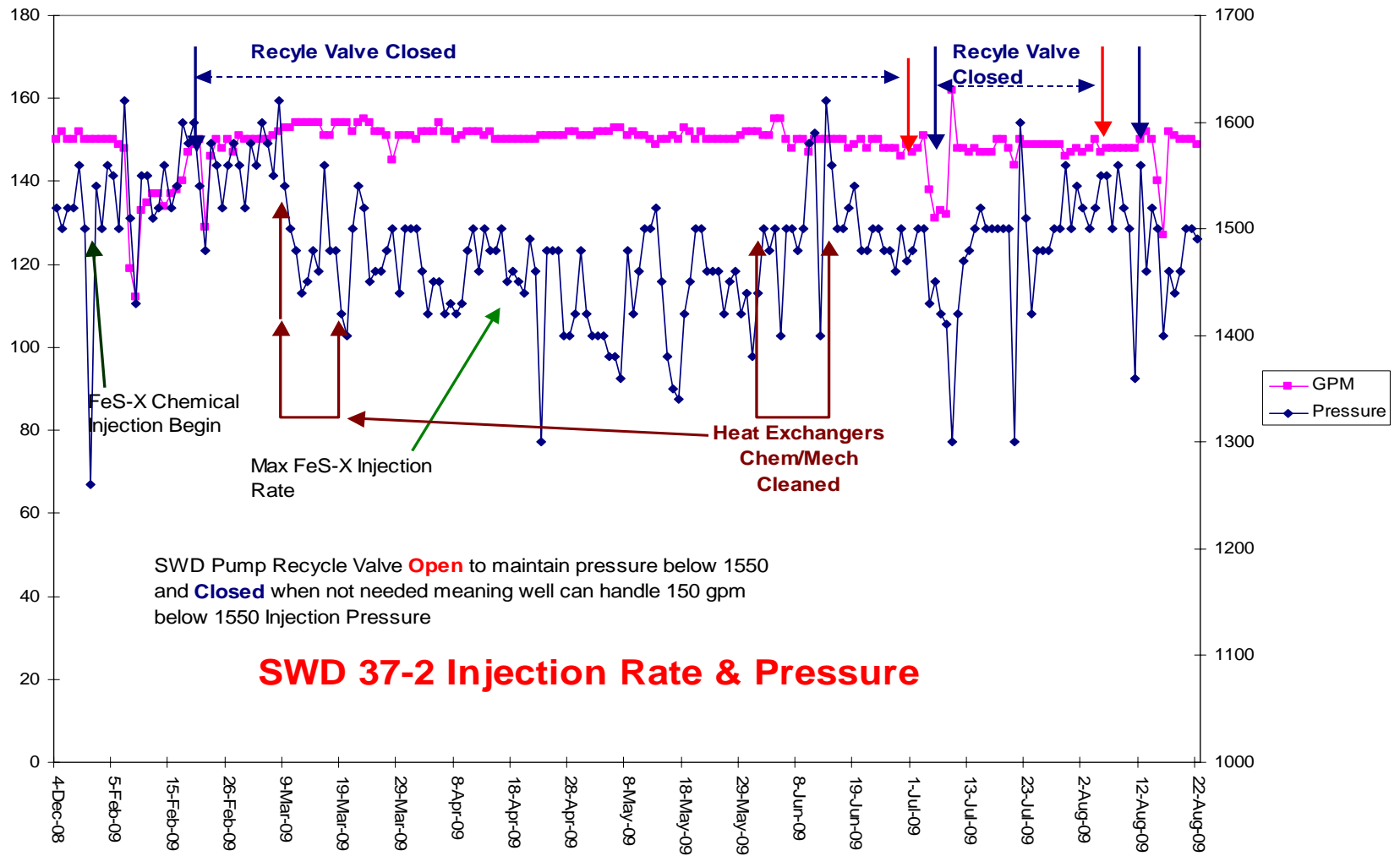
Figure 13: Fairway 8" Export Pipeline and incoming to Yellowhammer Gas Plant

Fairway 8" Pipeline					YH 8" PL
GRAIN SIZE DISTRIBUTION					
	MESH	MM	5/21/2009F	6/16/2009F	7/13/2009P
GRAVEL (2000+)	10	2.0000	0.0	0.0	0
VCRS SD (1000 - 1999)	18	1.0000	0.0	0.0	1.2
CRS SD (500 - 1000)	35	0.5000	4.6	0.0	10.4
MED SAND (250 - 499)	60	0.2500	18.4	0.0	27.9
FINE SAND (125 - 249)	120	0.1250	20.3	6.6	23.9
VFINE SAND (62 - 124)	230	0.0620	14.3	18.1	8.2
CRS SILT (31 - 61)	500	0.0310	11.4	16.7	4.7
MED SILT (16 - 30)		0.0160	9.1	13.9	4.8
FINE SILT (8 - 15)		0.0078	6.0	10.8	4.3
VFINE SILT (4 - 8)		0.0039	3.8	10.6	3.4
CLAY (1 -4)		0.0010	11.9	23.3	11.2
			100.0	100.0	100.0

So the challenge is to manage most of the solids upstream of the disposal well as far upstream in the system as reasonably possible. The clays may not be as big as an issue but the jury is still out as to managing the range of solids sizes.

As we stated in the project problem description in item number 2, being able to inject water at 150 gpm and below 1550 psi was a goal. Figure 14 shows that this was achieved when an effective amount of the FeS-X chemical could reach the perforations in the disposal well. A recycle valve from the disposal pump discharge was installed previously to allow pressure to be maintained under the regulated 1550-psi injection pressure. This water was routed back to the tank. As indicated in Figure 14, when the recycle was closed, we could stay below the max pressure at the 150-gpm-injection rate ranging from 4 – 6 hours.

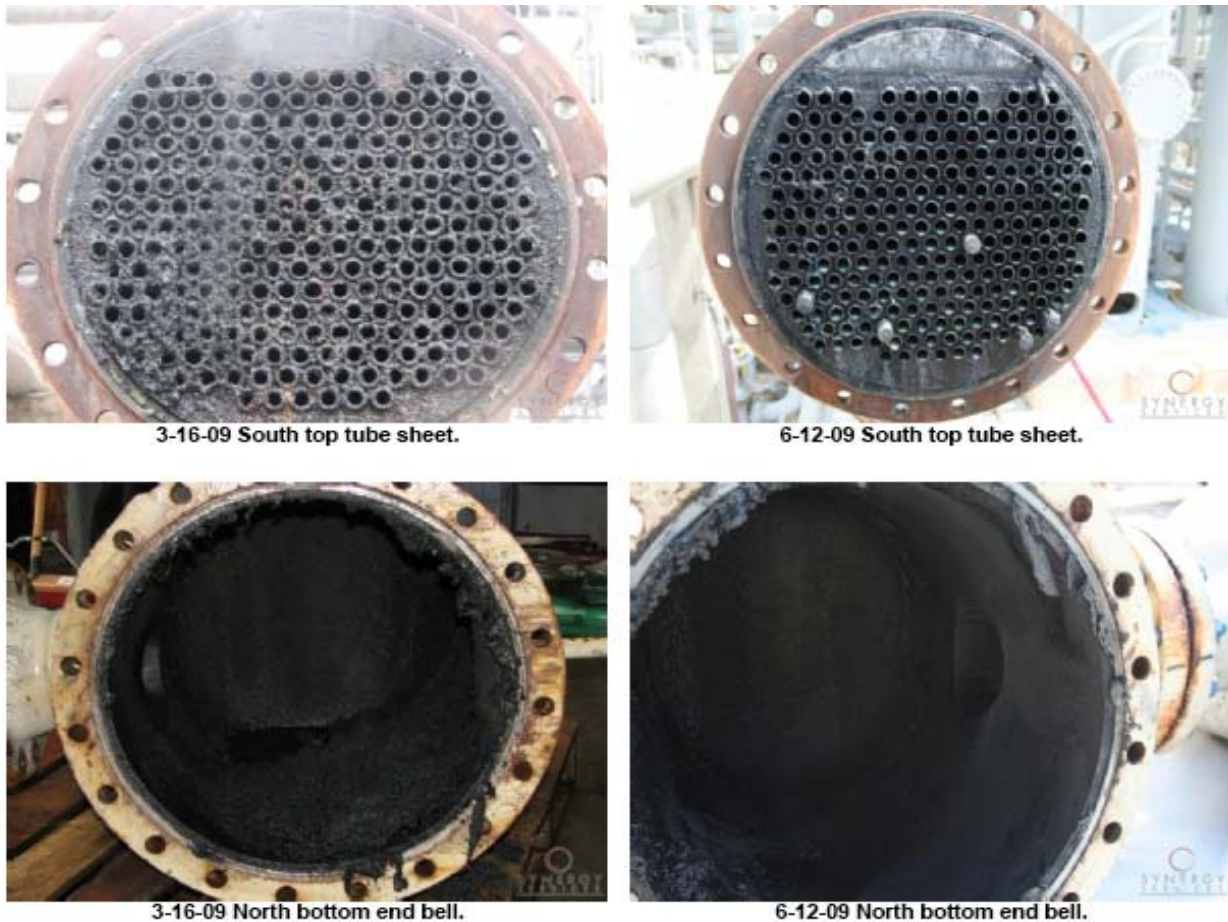
Figure 14: Rate and Pressure monitoring of the injection well



IV. FeS-X affect on the Sour Water Heat Exchangers

On two occasions during this period of time the heat exchangers were chemical cleaned on the shell side and mechanically cleaned on the tube side. Figure 15 shows the visual appearance of the same exchanger heads one month after FeS-X chemical injection and after five months. You can see how much cleaner the exchangers are and how the chemical is trying to continuously clean up the exchanger. Prior to adding this product, a mechanical cleaning was always required on the tubes whereas after the program was started, the plant operators could by-pass the exchanger and run steam condensate water through the exchangers and come back online.

Figure 15: FeS-X chemical injection through sour water exchangers



V. Conclusions

- FeS-X suite of chemical products can be effective to address issues where solids are bound by iron sulfide in pipelines, vessels and wells. These products can also be tailored to inhibit scale and address corrosion.
- Solids continue to plug the sour water exchangers but the primary contributing factor is low velocity. A solids removal system is needed upstream of the exchangers.
- Synergy FeS-X chemical online provides alternative if other options are not available to dispose of sour water at the regulated pressure and designed pump rate.

VI. Future Work:

- Test surplus equipment to quantify solids during maintenance pigging
- Test the performance of chemical treating to improve the performance of solids removal system
- Assemble data, analyze and recommend final solids removal design up front in the system
- Address issue with filtration system upstream of disposal pump after completion of solids removal system installation
- Continue to look at ways to address the intermittent water sources to the wastewater tank.

VII. Recognitions to:

- a. Shell Yellowhammer Operations, Mobile, AL for testing new products
- b. Synergy Services Inc., Magnolia Springs, AL, for exhaustive sampling and monitoring
- c. Champion Technologies, Laurel, MS District assisting with water samples
- d. Mycelex Technologies Corporation, Gainesville, GA, for technical support in sour systems
- e. ASKCo Instrument Company, Houston, TX, for new Millipore sampler design