

# Sulfur Unit Equipment Problems and Low Silicon Carbon Steel Corrosion

Gerald W. Wilks  
Lemont Refinery  
CITGO Petroleum



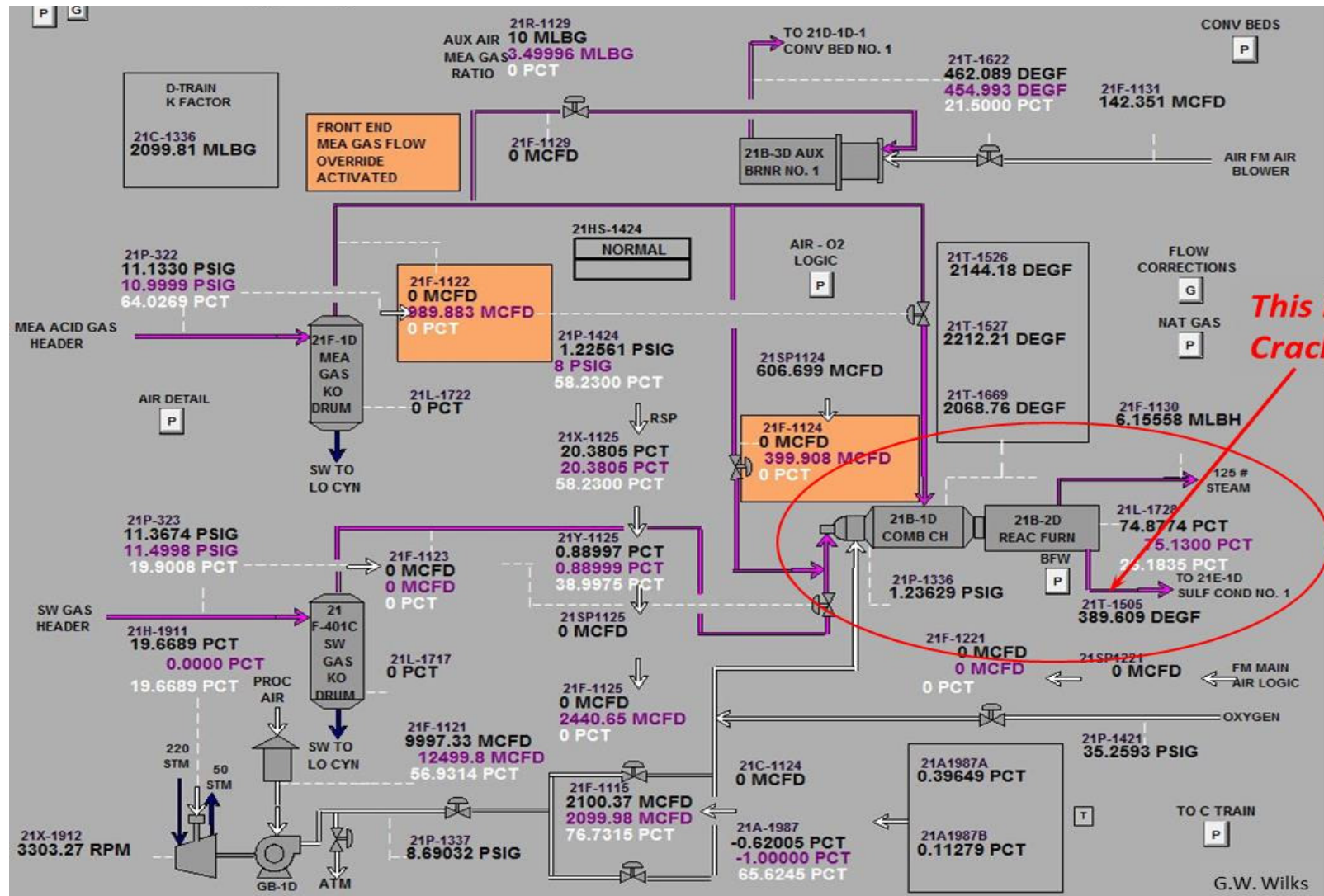
# Summary

- Weld cracking in piping connecting a reaction furnace and sulfur condenser
- Innovative repairs used to get a Sulfur Unit back in-service
- Refractory failure in a reaction furnace and resulting corrosion
- High temperature sulfidic corrosion of low silicon carbon steel
  - ✓ Chevron's Crude Unit failure - August 6, 2012, Richmond, CA
  - ✓ BP's FCC slurry line failure – February 18, 2003, Whiting, IN
  - ✓ Description of the Whiting failure
  - ✓ Testing done to determine the cause of the unusual corrosion
  - ✓ Graph showing the low silicon effect on corrosion
- Conclusions

# Weld Cracking in Piping Connecting Two Vessels

- Failure occurred in November, 2012 in piping connecting 21B-2D and 21E-1D on D-Train of the Sulfur Unit
- 21B-2D is a reaction furnace and 21E-1D is a sulfur condenser
- The leak caused D-Train to shut down
- The vessel was cooled, purged, filled with nitrogen, and repairs were made externally using alloys that would not corrode in-service
- The repair was done safely and the vessel remained fit-for-service until the next turnaround when a permanent repair was made
- Other reactor–condenser connections with similar designs were analyzed and modified to prevent fatigue failures.

# Where the Failure Occurred – In a Reaction Furnace

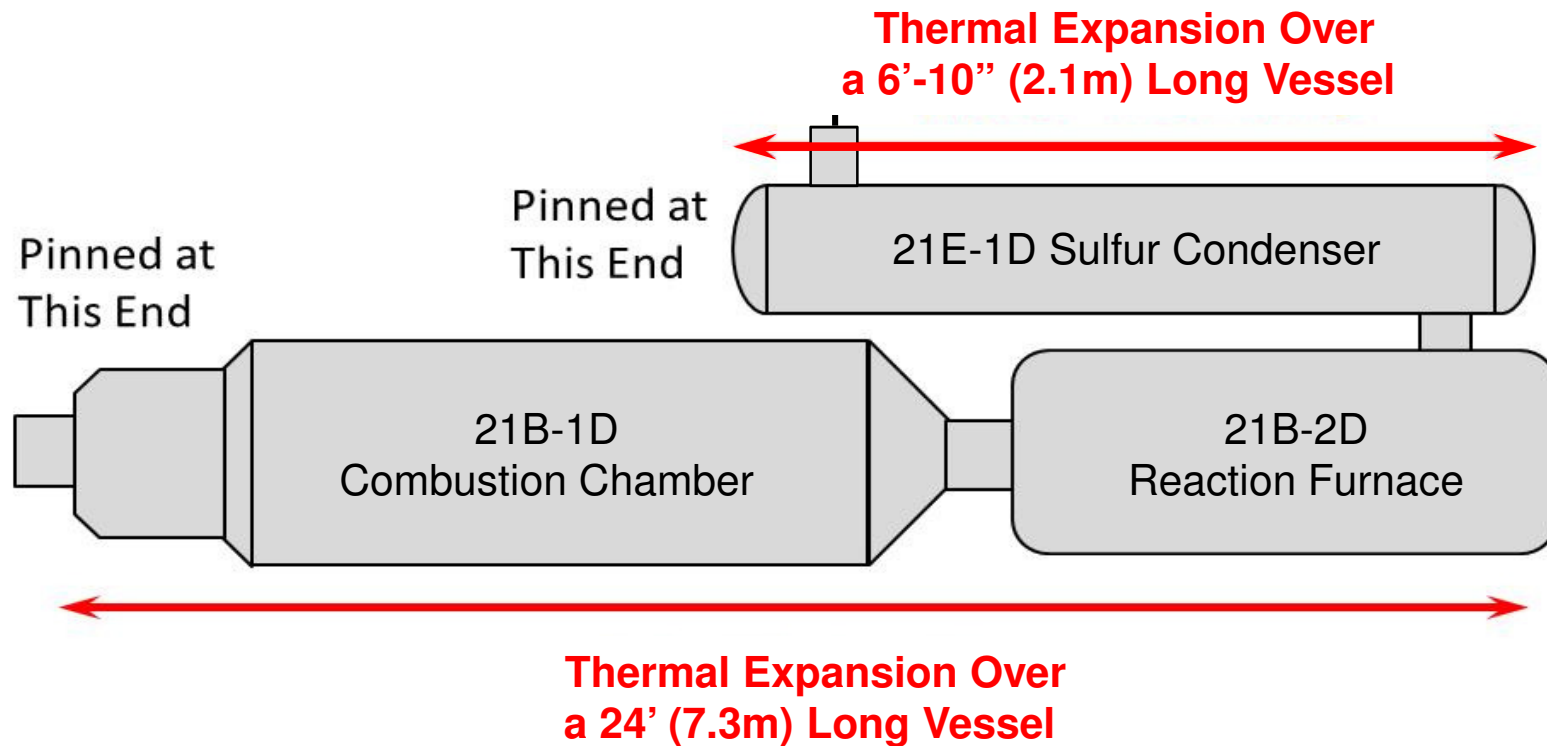




## Photo of the Cracking – It Followed the Weld Toe



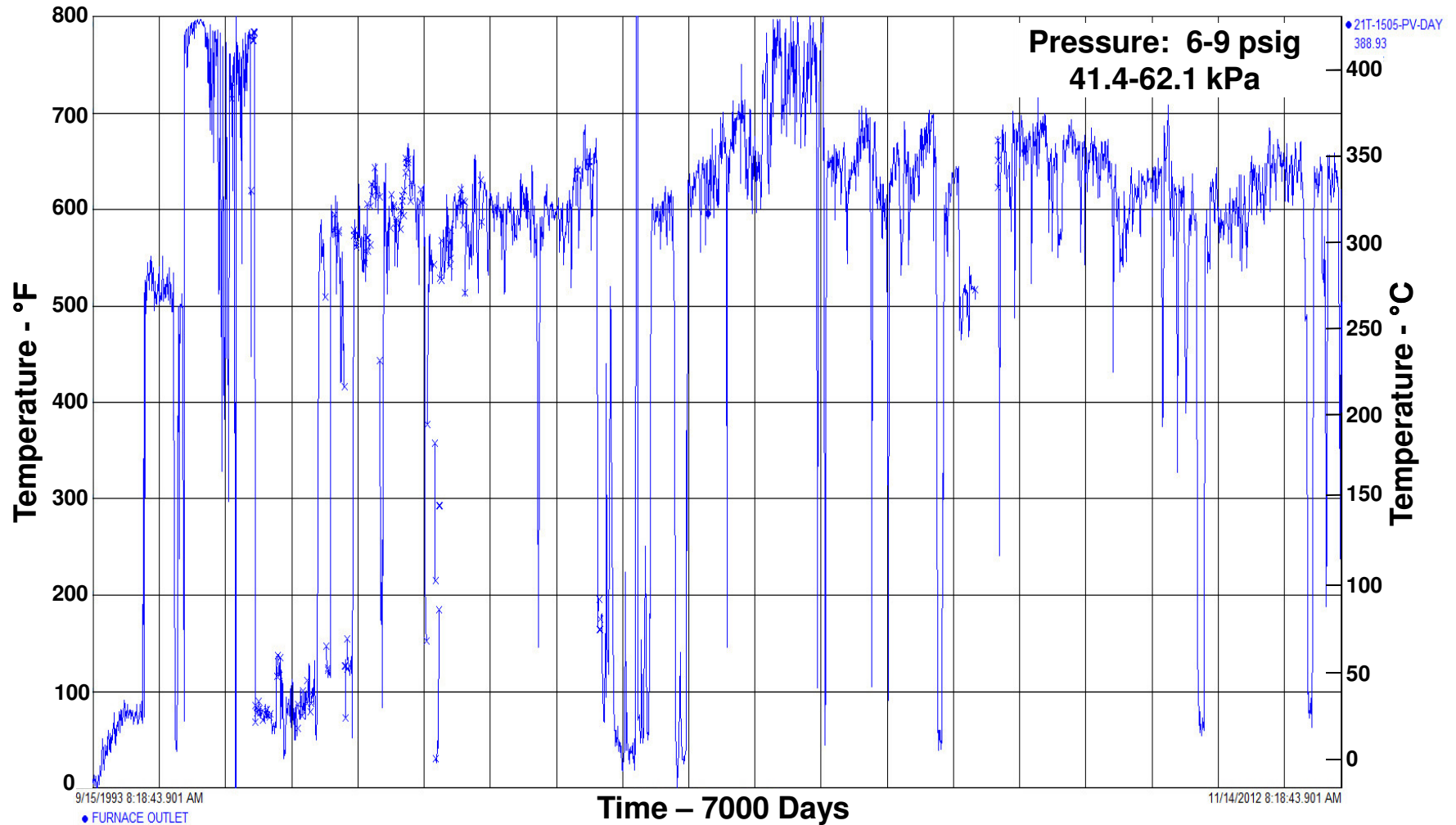
## **What Caused the Cracking**



*The relative motion due to the different amounts of expansion resulted in high bending stresses at the pipe attachment welds.*

# Pipe ID Temperature and Pressure

*The thermal stresses at the weld are high and there are enough cycles to start fatigue cracks.  
The small cycles also contribute to fatigue cracking if a high constant tensile stress is present.*



# D-Train Connecting Pipe Repairs

## Repair:

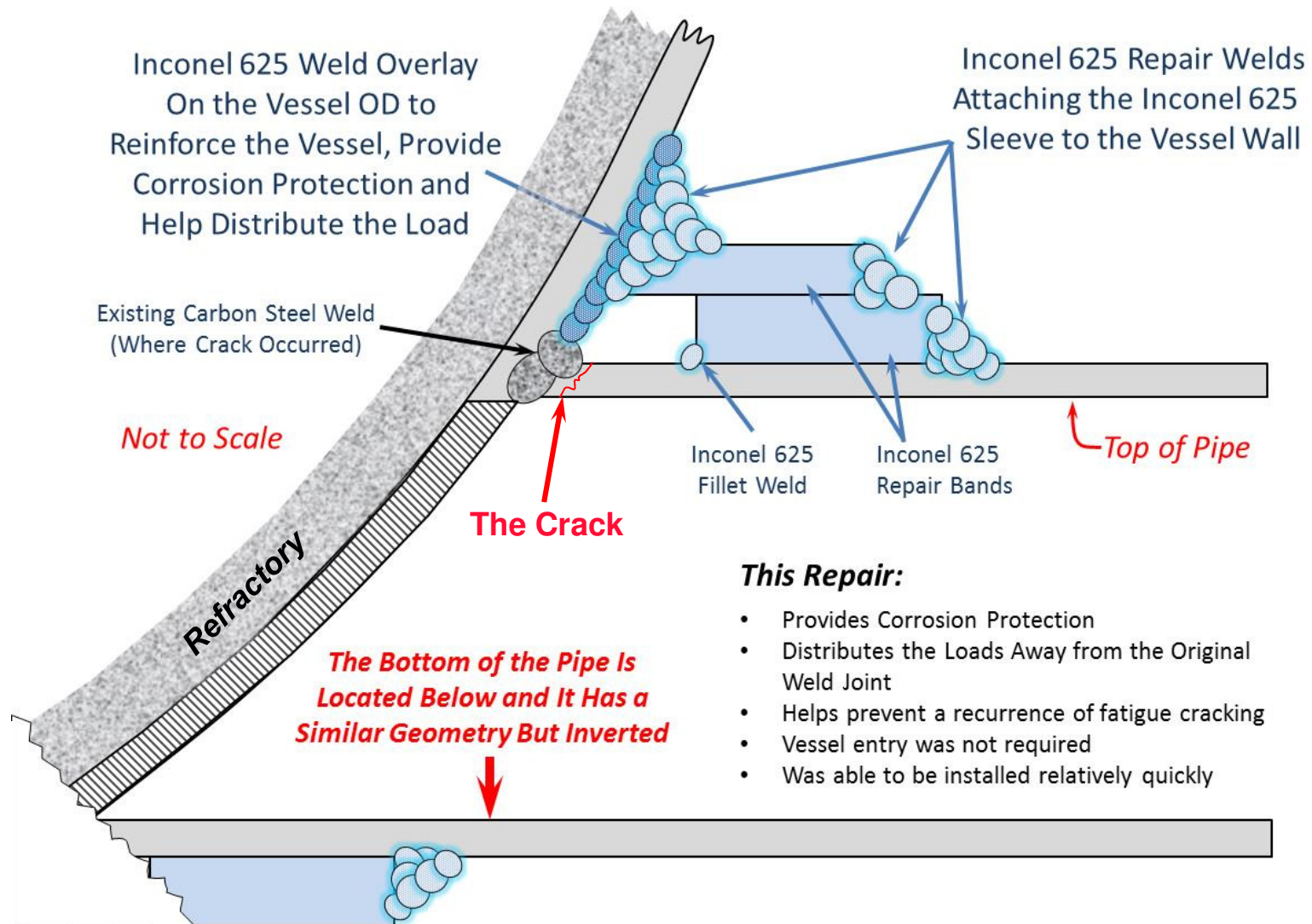
- A repair joint was designed using alloys that wouldn't corrode in service due to  $\text{H}_2\text{S}$  or  $\text{H}_2\text{SO}_4$
- Repair followed the guidelines in ASME PCC-2, Article 2.4, "Welded Leak Box Repair" – see the next slide
- Finite element analysis indicated this joint was stronger than the original joint
- Equipment with similar connections was UT shearwave inspected
- After the fact API 579 analysis indicated repairs were fit-for-service

## Next Turnaround:

- The Inconel 625 repair was removed
- The connecting pipe was replaced and a new pipe with reinforced connections at both vessels was installed
- Inspected and replaced the similar piping on C-Train
- Sulfur condenser pinning was revised



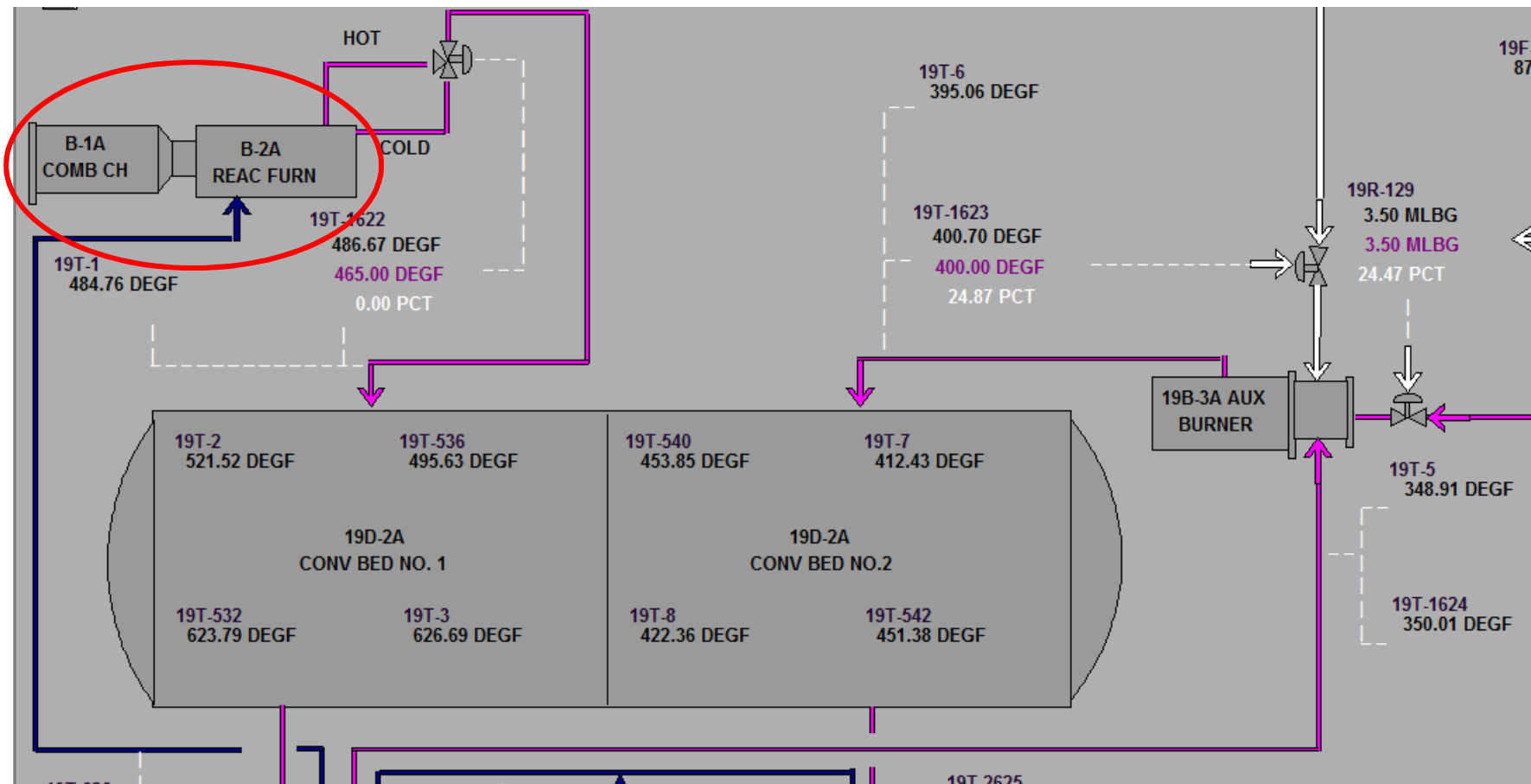
# Sketch of the Welded Leak Box Repair



# Reaction Furnace Refractory Failure and Corrosion

- Process Description
- Photograph of the vessel OD showing the overheated vessel wall
- Infrared photograph of the OD showing in-service temperatures
- Photographs of the internal refractory damage
- Close-up of the corrosion damage
- Actions taken as a result of this failure

# Problem Description – Hot Reaction Furnace Shell



The hot reaction furnace shell was noticed by Operators when it rained and infrared monitoring was used to determine the temperatures.

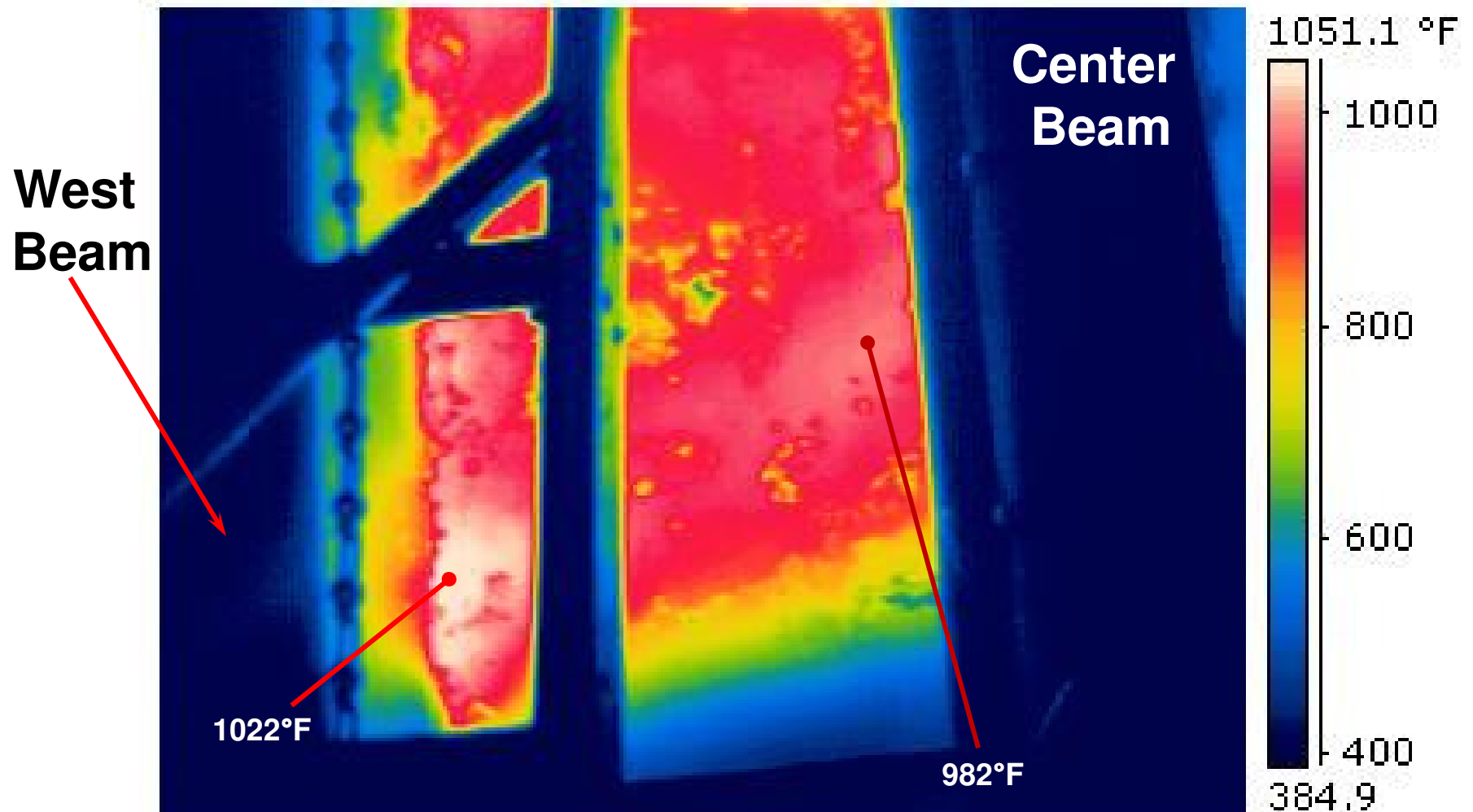


# What the Vessel Looked Like on the Outside



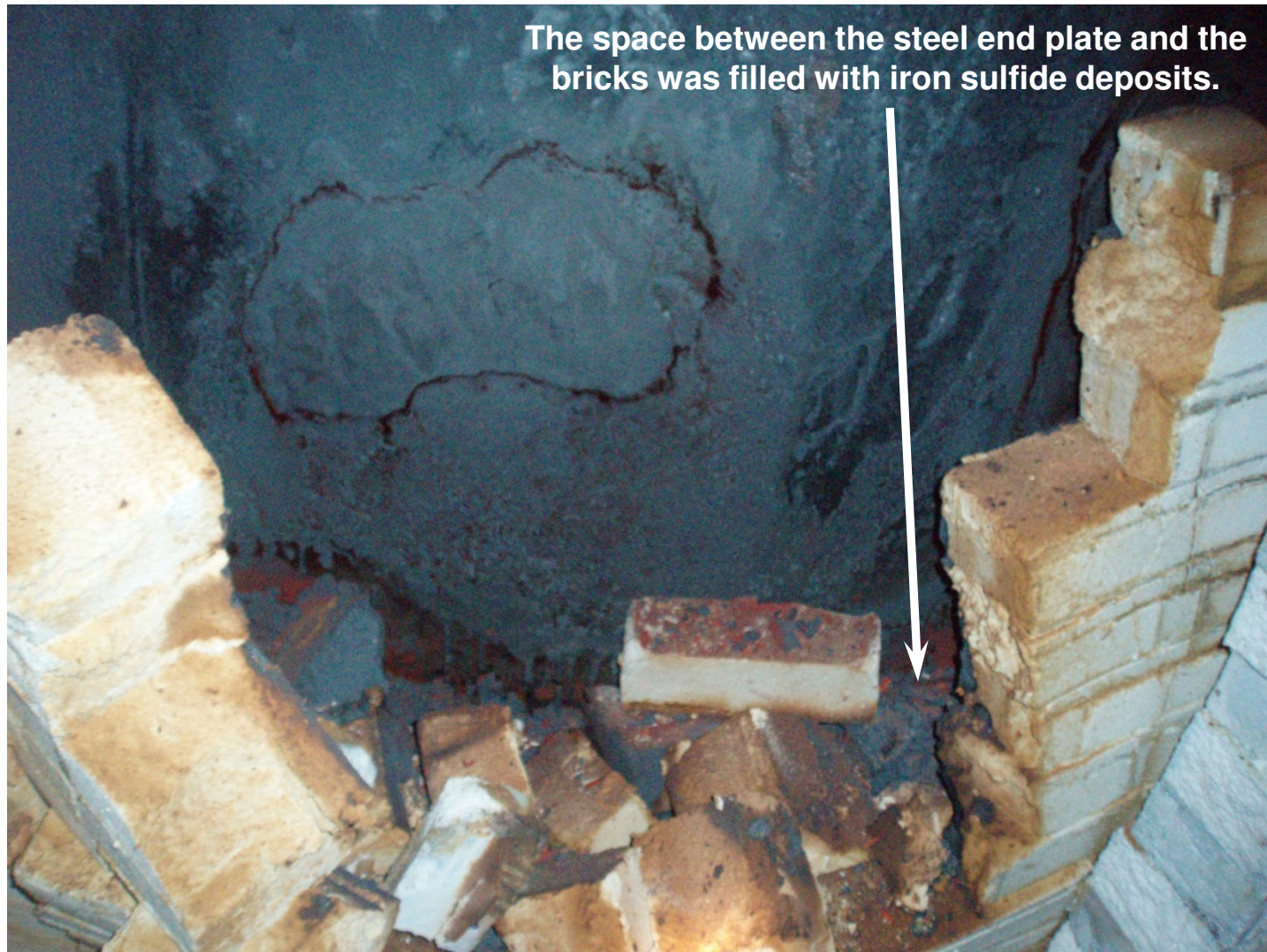
# IR Scan of the OD of 19B-2A Furnace

Steam lances were used to keep the wall temperature down, but unit shut down was eventually necessary.





# Refractory and Wall Damage on the ID





## Refractory and Wall Damage on the ID



## Refractory and Wall Damage on the ID



Failure occurred because the refractory bricks were set with castable refractory. This reduced the ability of the wall to expand so it bulged into the Reaction Furnace and cracked. Then resulting corrosion deposits pushed the wall inward causing the refractory to completely separate from the steel end plate.



## Close-Up of the Corrosion on the Wall



Corrosion deposits were a mixture of iron oxides and iron sulfides.

## Vessel Repairs and Other Actions Taken

- The 1½-Inch end plate was replaced.
- All refractory bricks installed with castable were removed
- New refractory was installed with gaps between the bricks to accommodate expansion.
- Infrared surveys were conducted on similar high temperature Sulfur Unit equipment
- UT thickness measurements were taken on similar Sulfur Unit equipment



# Sulfidic Corrosion of Low Silicon Carbon Steel

- Chevron had an expensive crude unit fire due to unexpected corrosion of low silicon carbon steel: SA-53 pipe with low silicon vs. SA-106 piping with normal silicon Refer to the CSB report
- First documented case of accelerated sulfidic corrosion of low silicon carbon steel was on a FCC at Whiting Refinery
- Description of the Whiting FCC piping failure
- Weld cross section showing the low silicon corrosion difference
- Corrosion deposits in low silicon and normal silicon carbon steel
- Testing done to develop a graph showing the effect of silicon on corrosion rate
- Conclusions

# Failure of Low Silicon Carbon Steel on a FCC





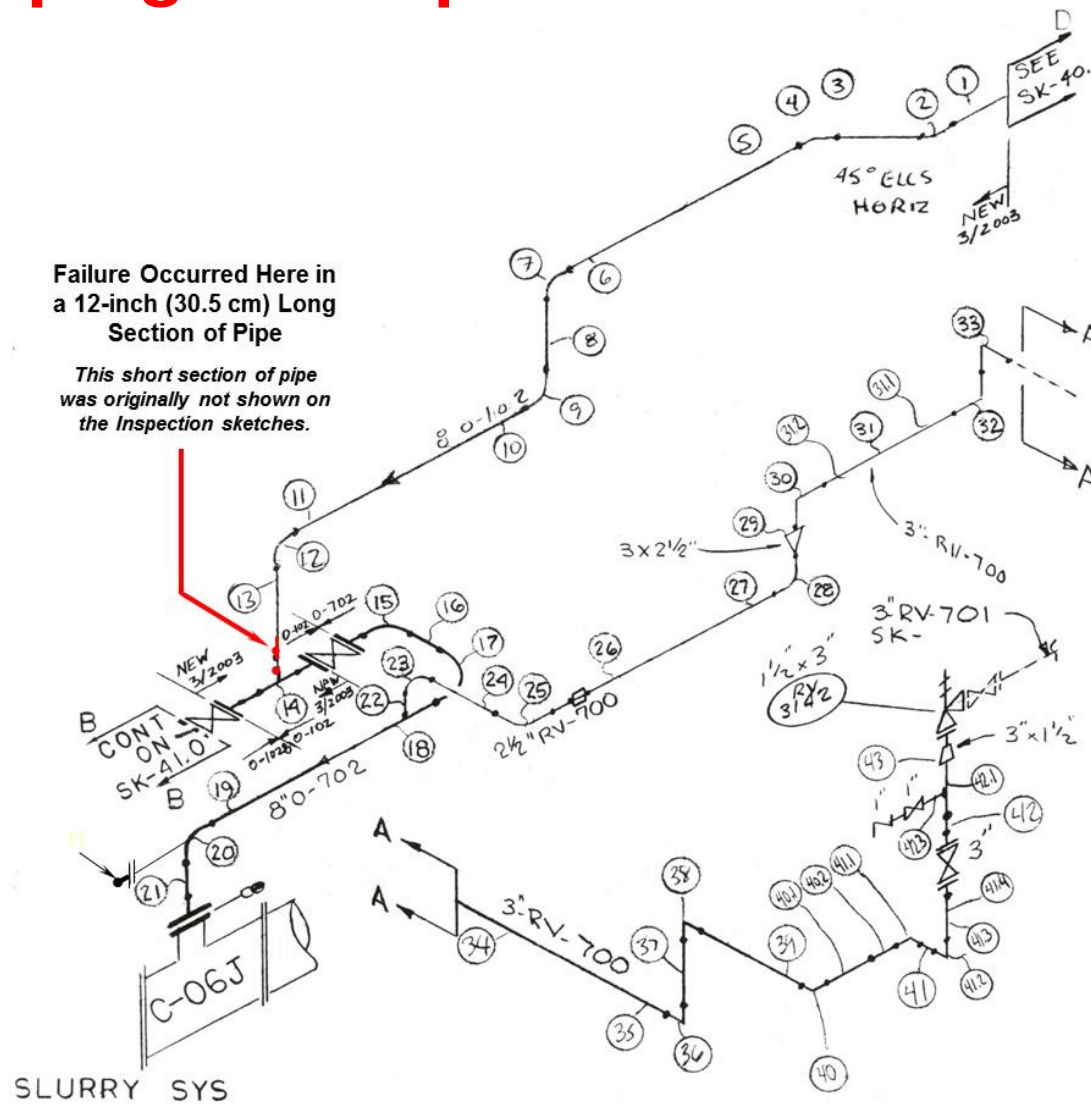
# Surprise Failure – Inspection Data Indicated No Problems

Fractionator Bottoms @ ~150 psig (1035 kPa) & 650-700°F (345-370°C)

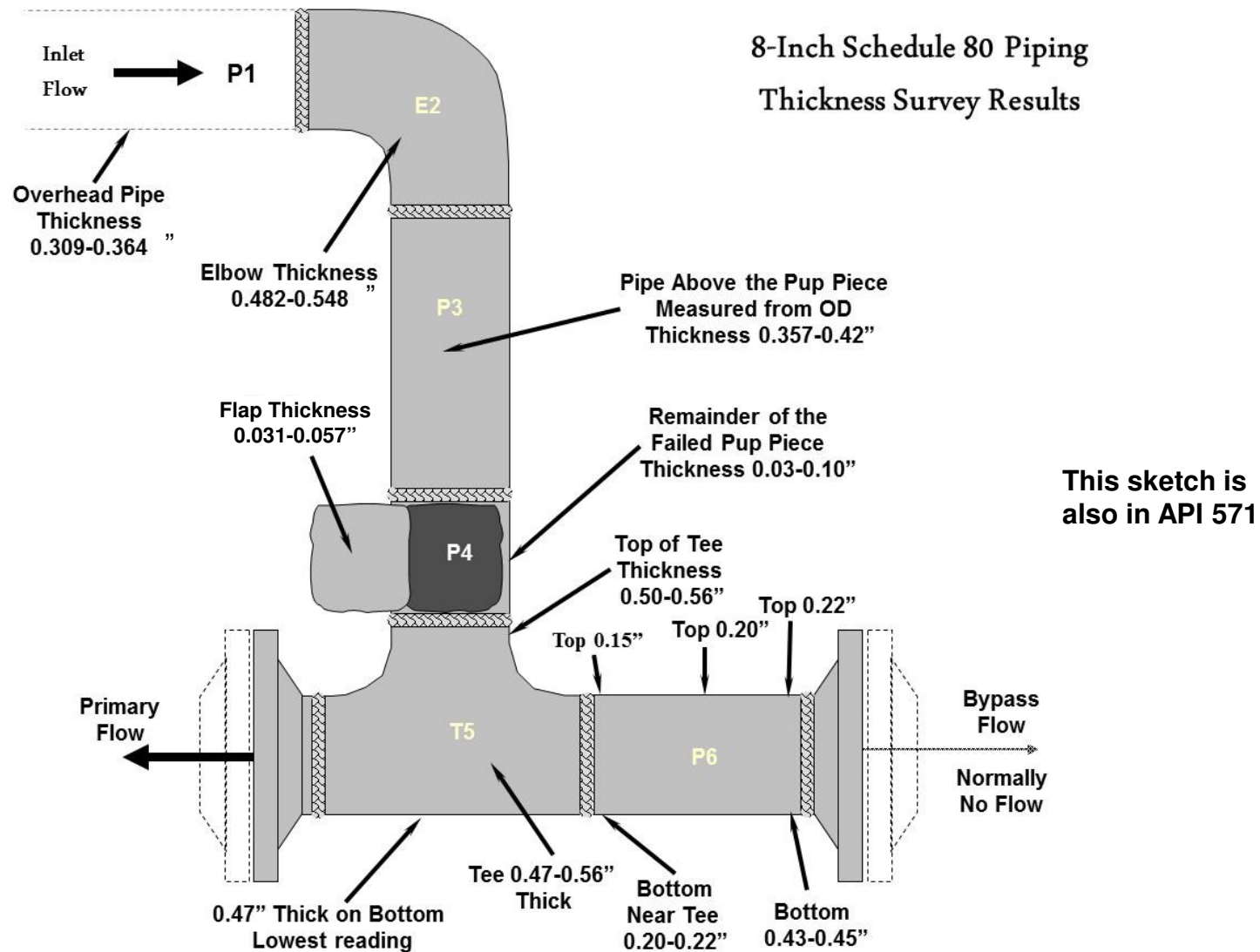


This photograph  
is also in API 571

## Piping Description and What Failed

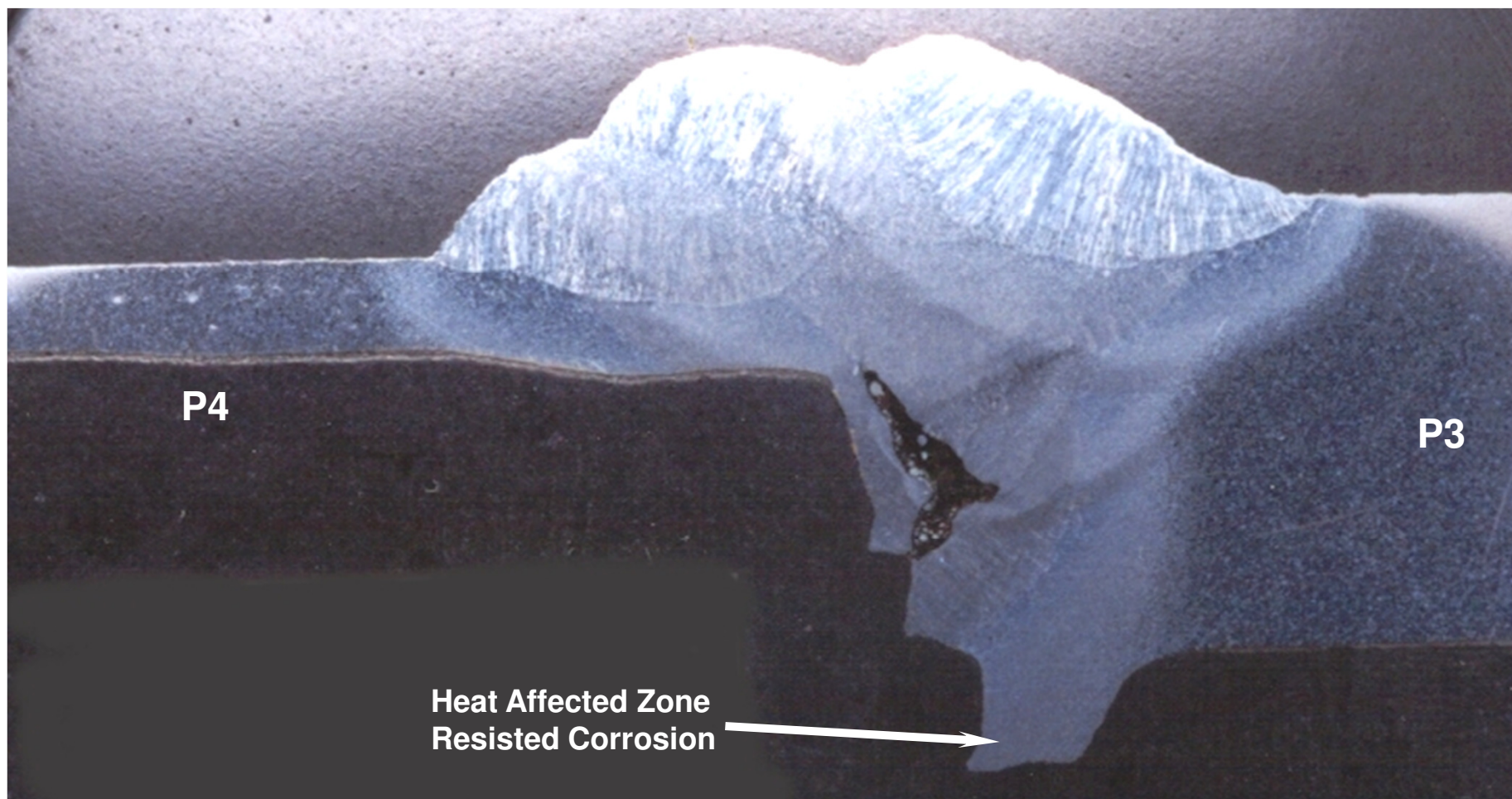


# The Pipe that Leaked and Nearby Piping

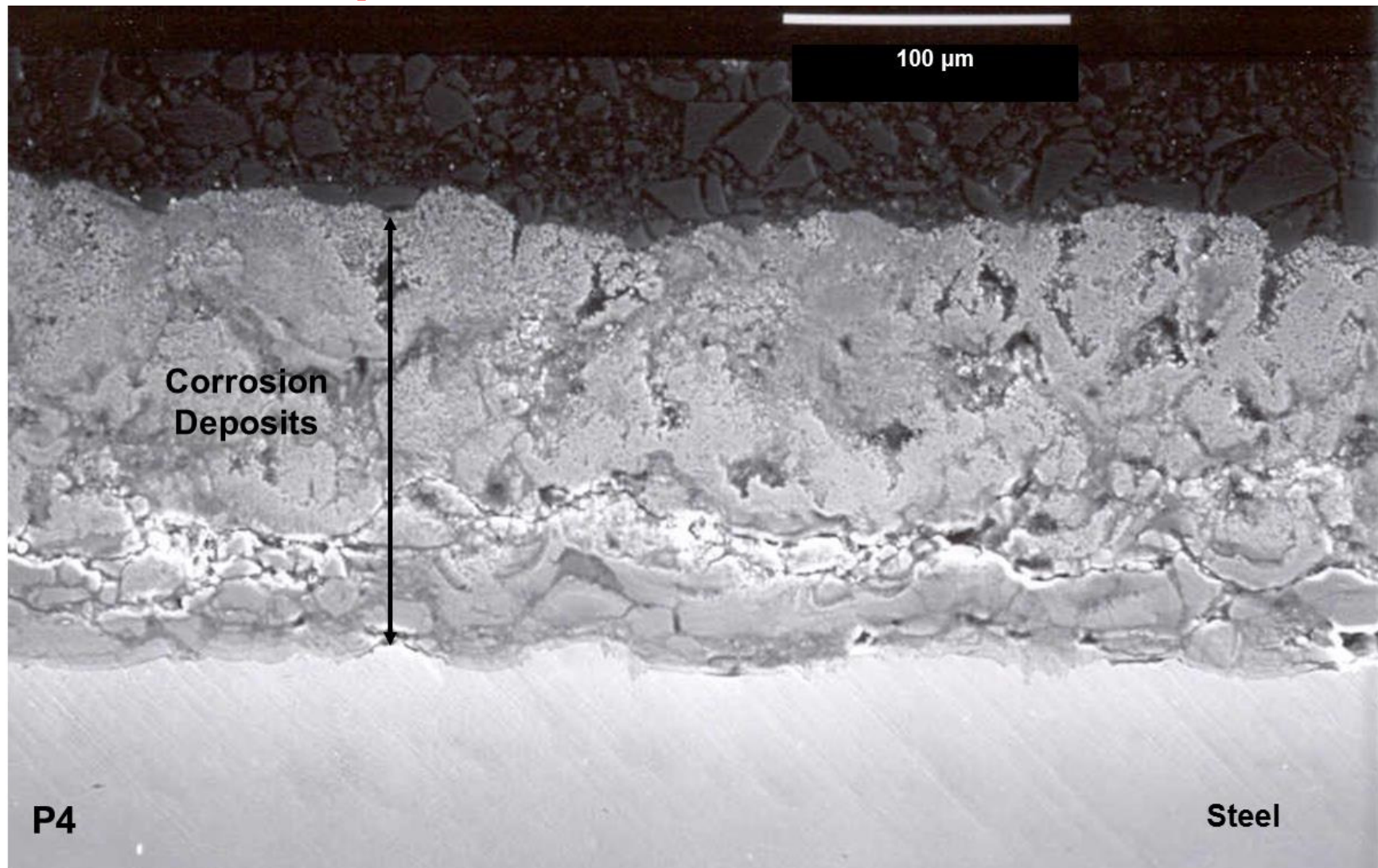




## Cross Section Through the Weld Between P3 and P4

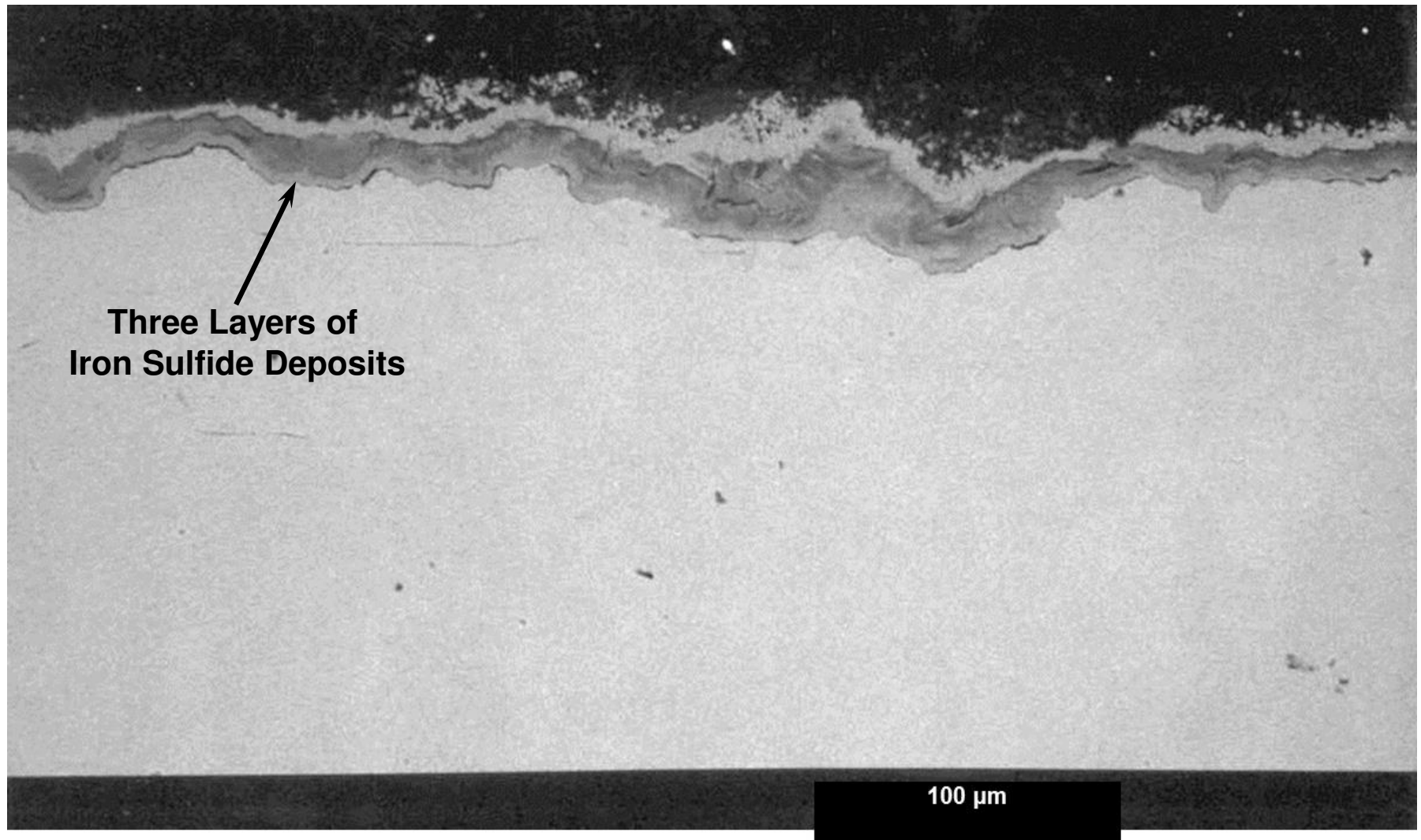


# Corrosion Deposits on the Low Silicon SA-53 Steel

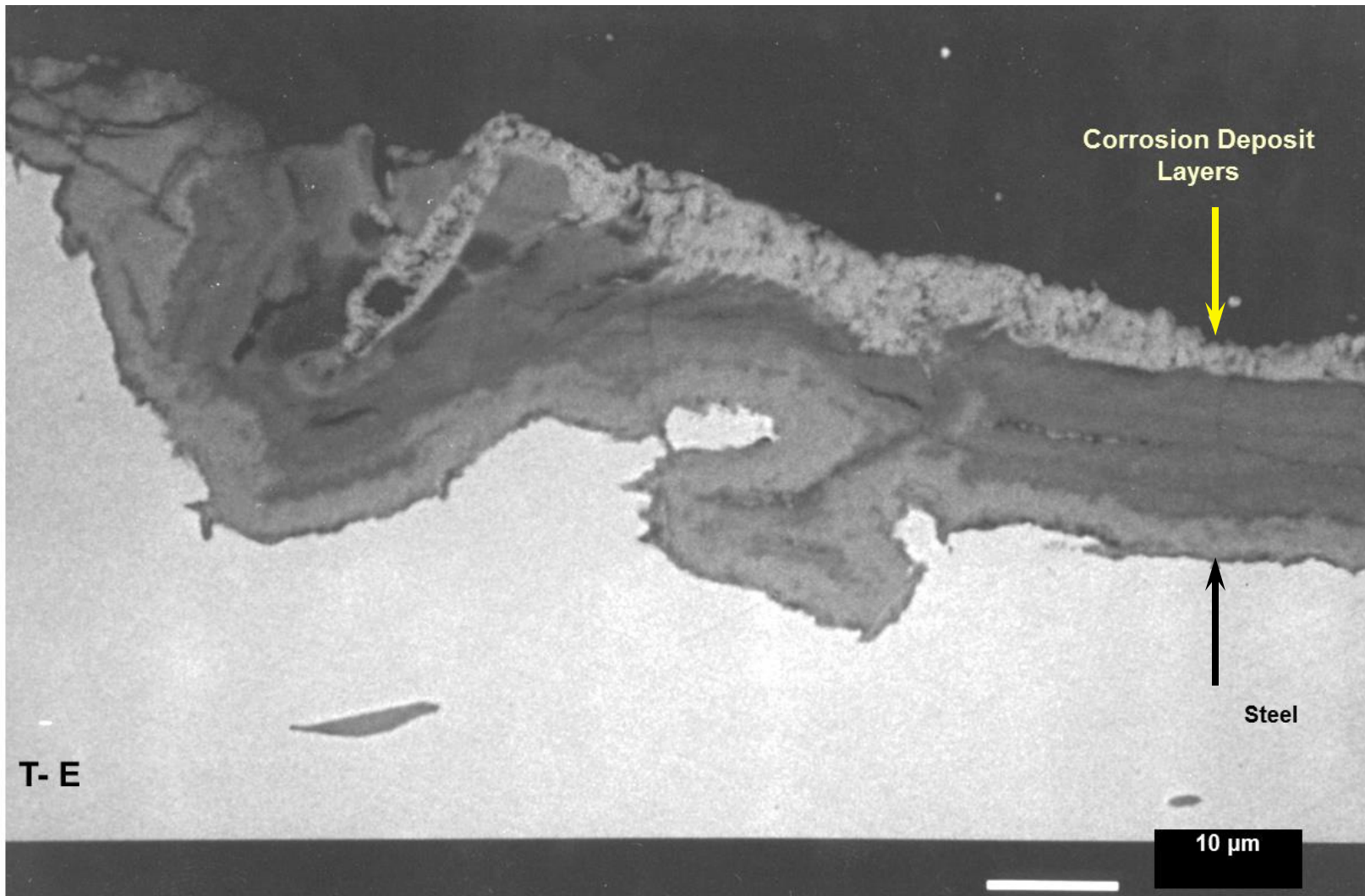




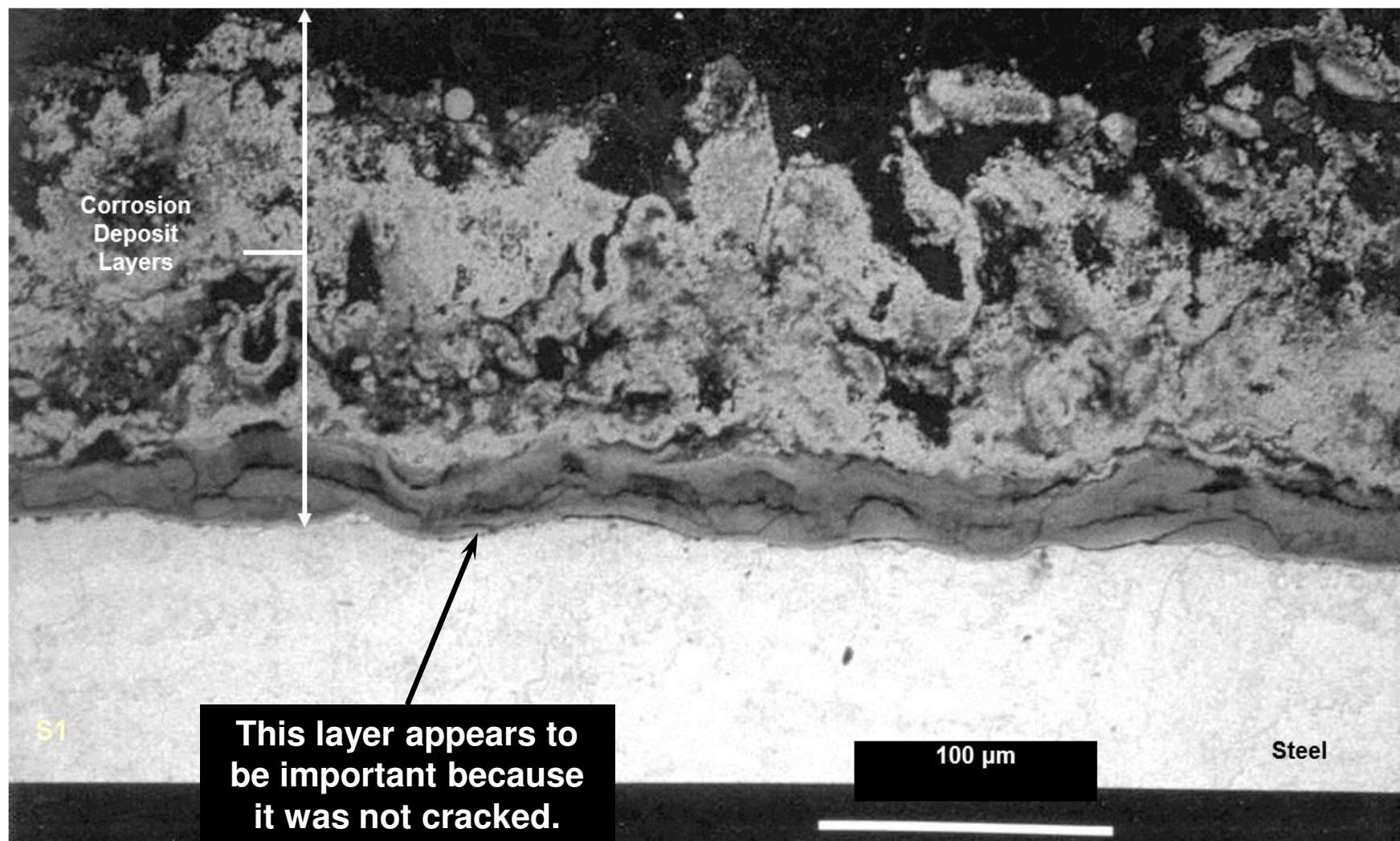
# Layered Corrosion Deposits on SA-106 Steel



# Layered Corrosion Deposits on SA-106 Steel



## Example of 0.07% Silicon – 4 Mils/Year Corrosion Rate



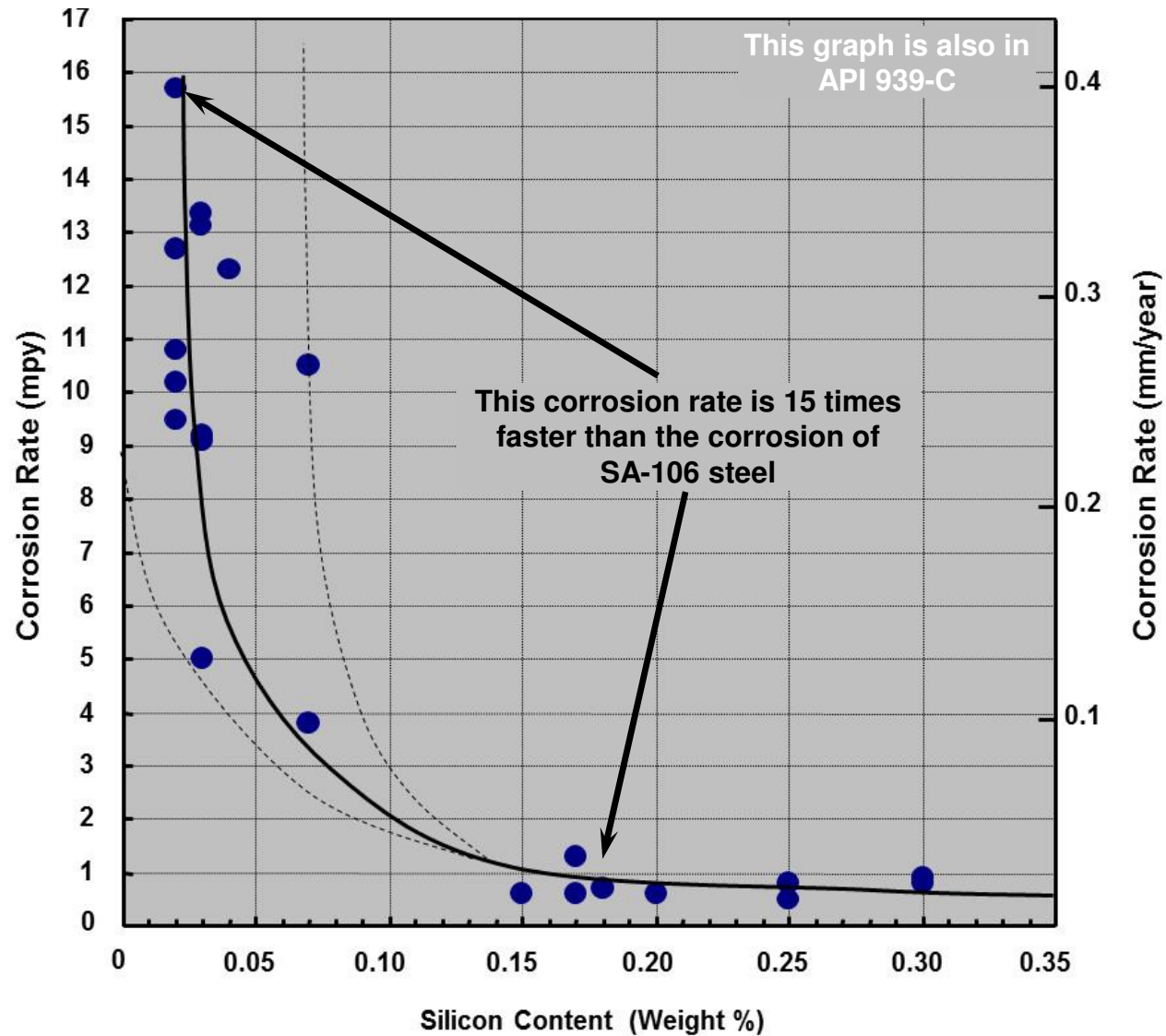


# Testing to Find Low Silicon Pipe in the FCC

Results of Chemical Analyses of Piping Samples from FCU 500 Slurry System (Weight %)																	
Sample ID	Maximum Corrosion Rate (mpy)	C	Mn	P	S	Si	Ni	Cr	Mo	Cu	Al	V	Nb	Ti	N	O	Other
P1	5.0	0.26	0.71	0.007	0.009	0.03	0.02	0.01	<0.01	0.01	0.01	----	----	----	0.0052	0.044	----
E2	0.5	0.15	0.46	0.016	0.011	0.25	0.02	0.02	<0.01	0.02	<0.01	----	----	----	----	----	----
P3	3.8	0.23	0.84	0.007	0.014	0.07	0.04	0.07	0.05	0.07	0.03	<0.01	<0.01	<0.01	0.0124	0.039	Sn-0.01
P4	12.3	0.24	0.72	0.005	0.022	0.04	0.02	0.02	<0.01	0.02	0.03	<0.01	<0.01	<0.01	0.0041	0.037	----
T5	0.8	0.25	0.76	0.014	0.033	0.25	0.05	0.04	0.01	0.06	<0.01	<0.01	<0.01	<0.01	<0.0005	0.011	----
P6	9.2	0.24	0.73	0.006	0.025	0.03	0.02	0.03	<0.01	0.02	0.03	----	----	----	----	----	----
R1-P	13.2	0.23	0.55	0.005	0.016	0.03	0.02	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	----	----	----
R1-E	0.8	0.18	0.58	0.016	0.02	0.30	0.03	0.02	<0.01	0.02	0.03	<0.01	<0.01	<0.01	----	----	----
R2-E	0.9	0.18	0.59	0.017	0.02	0.30	0.03	0.02	<0.01	0.02	0.03	<0.01	<0.01	<0.01	----	----	----
R2-P	12.7	0.24	0.54	0.005	0.015	0.02	0.02	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	----	----	----
Q1-P	13.1	0.23	0.54	0.005	0.014	0.03	0.02	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	----	----	----
Q1-E	0.6	0.16	0.59	0.022	0.012	0.17	0.04	0.02	<0.01	0.02	0.03	<0.01	<0.01	<0.01	----	----	----
Q2-E	0.7	0.16	0.59	0.022	0.013	0.18	0.04	0.02	<0.01	0.02	0.03	<0.01	<0.01	<0.01	----	----	----
Q2-P	15.7	0.22	0.54	0.006	0.013	0.02	0.02	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	----	----	----
T-P	10.8	0.23	0.66	0.005	0.019	0.02	0.02	0.01	<0.01	0.03	0.03	<0.01	<0.01	<0.01	----	----	----
T-E	0.6	0.20	0.74	0.012	0.016	0.15	0.12	0.09	0.05	0.18	0.03	----	----	0.03	----	----	----
U1	10.2	0.22	0.56	0.005	0.016	0.02	0.02	0.05	<0.01	0.02	0.02	<0.01	<0.01	<0.01	----	----	----
U2	9.5	0.21	0.59	0.005	0.019	0.02	0.02	0.01	<0.01	0.02	0.03	<0.01	<0.01	<0.01	----	----	----
S1	10.5	0.25	0.72	0.005	0.015	0.07	0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	----	----	----
S2	1.3	0.24	0.73	0.009	0.013	0.17	0.01	0.02	0.01	<0.01	0.01	<0.01	<0.01	<0.01	----	----	----
F1	9.1	0.25	0.58	0.006	0.019	0.03	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	----	----	----
F2	0.6	0.19	0.60	0.010	0.015	0.20	0.02	0.02	<0.01	0.03	0.02	<0.01	<0.01	<0.01	----	----	----

Carbon steel piping on some other units at Whiting was inspected to identify low silicon carbon steel. In 2015 Lemont Refinery completed inspecting all carbon steel piping operating above 425°F (218°C).

# Corrosion Rate vs. Silicon Content for Piping



# Conclusions

- Due to the high temperatures in sulfur units, expansion of equipment needs to be taken into account.
- Expansion of refractory also needs to be accounted for in equipment design. Castable refractory is sometimes a problem.
- Low silicon carbon steel (SA-53) can corrode at a rate that could be 15 times the rate that normal silicon carbon steel (SA-106) corrodes.
- Not all SA-53 pipe has low silicon content. Also silicon content isn't always present in the steel – some Si is present in silicate inclusions.
- Many refineries are conducting programs to identify low silicon carbon steel in systems operating above 425°F (220°F). Some use >450°F (232°C) instead.
- Low silicon carbon steel can be found with chemical analyses and with thickness measurements. Low silicon is less than 0.10 weight %.
- Forged piping components and alloys usually have sufficient silicon content to avoid this kind of accelerated sulfuric corrosion.