

MOTIVA PAMC Sulfiding Low Temperature TGTU Catalyst

| <u>Team Members</u> | <u>Special Thanks</u> |
|---|--|
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Port Arthur Manufacturing Complex Sulfiding Low Temperature TGTU Catalyst

Abstract

In November 2023, Motiva performed the TGTU sulfiding procedure presented and discussed at Brimstone 2023 by ASRL, Rob Marriott, Chris Lavery, and Michael Huffmaster. This Sulfiding Procedure for Low Temperature TGTU Catalyst utilizes the sulfiding reaction exotherm while also preventing H₂S starvation in the lower part of the reactor bed while sulfiding. With Reactor Inlet Temperature at ~165°F, sulfiding H₂S (acid gas) was first introduced observing an exotherm followed by the introduction of H₂. Reactor Inlet Temperature was then slowly ramped up while controlling the sulfiding exotherm with changes in sulfiding AG flow and H₂ flow. With Reactor Inlet Temperatures in the 300-315°F range, the desired 575-600°F reactor bed temperatures were achieved thus completing the sulfiding steps. Performance of the TGTU Reactor has been very good since startup.

Background

The Motiva Port Arthur Refinery is part of the Port Arthur Manufacturing Complex processing over 650 MBPD of crude oil and total of >725 MBPD of feedstocks making it the largest Refinery in the Americas and 7th largest in the world. The Sulfur Processing Facility is one of the largest in the world that is part of a Refinery at ~2500 LTPD. There are 6 SRU’s and 5 TGTU’s processing the Sulfur for the Refinery’s requirements.

To improve energy efficiency, the 5 TGTU’s have been changed out from C234 to either C834 or C934 during the latest turnarounds. C934 has been installed once it was commercially available. The oldest TGTU’s (TGTU1 and TGTU2) also have a combination of steam preheater with hot oil heater. The newest TGTU’s use 600 psig superheated steam for preheat.

The C934 Low Temperature Catalyst offers the potential to shutdown the Hot Oil Heaters on TGTU1 and TGTU2 due to the lower Reactor Inlet Temperature (RIT) requirements. Catalyst sulfiding and end-of-life

RIT requirements may need the Hot Oil Heater to remain in service or change the heater to 600 psig superheated steam as another option.

Brimstone 2023 included presentations and research papers by ASRL, Rob Marriott, Chris Lavery, and Michael Huffmaster discussing an alternative catalyst sulfiding procedure that could utilize the TGTU Catalyst Sulfiding Exotherm to assist the TGTU Reactor Preheater in providing the required duty/temperature for sulfiding. This approach could also potentially prevent H₂S starvation in the bottom of the bed while sulfiding thus improving catalyst activity after sulfiding.

After discussions internally and with ASRL, this alternative approach was approved for the oldest and smallest TGTU1 Catalytic Reactor. TGTU1 receives SRU Tail Gas from two SRU's using a combination of steam preheat exchanger and hot oil heat exchanger.

In November 2023, the sulfiding of the TGTU1 Low Temperature Catalyst was successfully performed with the procedure discussed at Brimstone 2023. With low RIT of ~165°F, H₂S was first introduced (acid gas) observing an exotherm. Once complete, H₂ was added while controlling the exotherm. RIT was then slowly ramped up to the 300-315°F range. The desired 560-615°F reactor temperature profile was achieved and held for 5-6 hours thus achieving the complete sulfiding steps. Performance of the TGTU Reactor has been very good since startup.

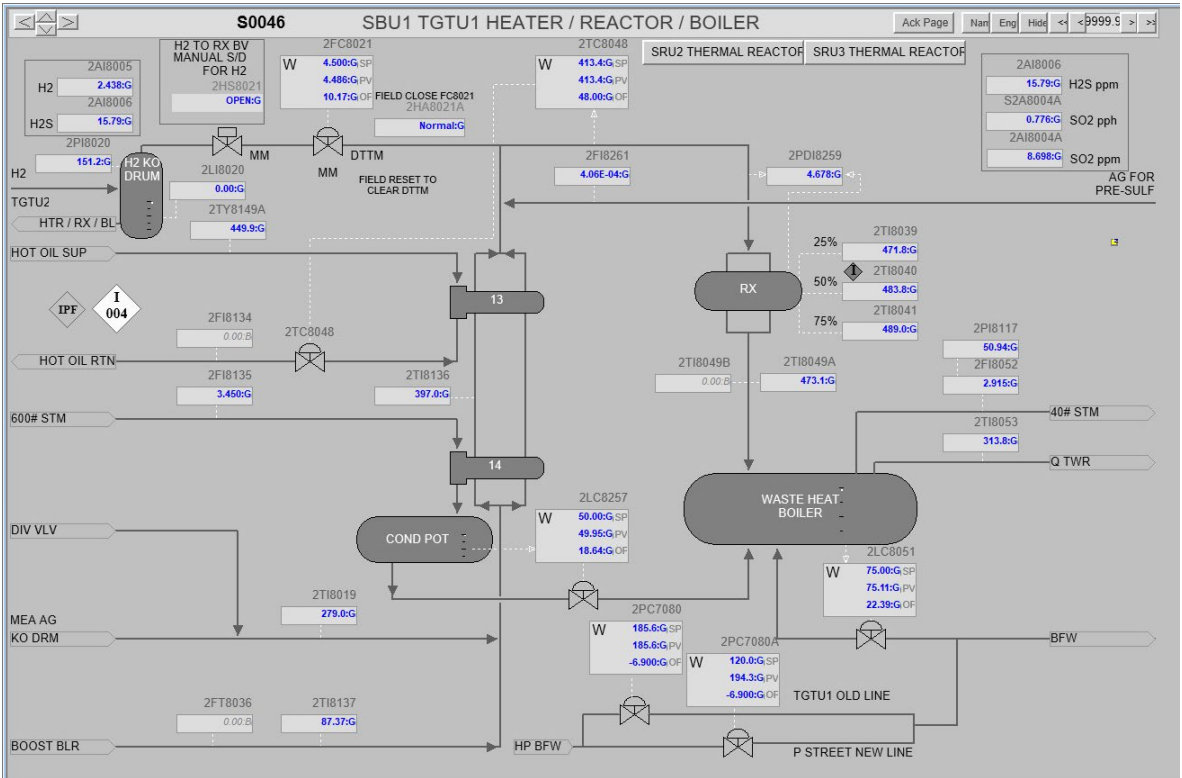
Sulfiding Low Temperature TGTU Catalyst – Lessons Learned

There were two attempts of the Low Temperature Sulfiding Procedure with H₂S and H₂. The second attempt was very successful.

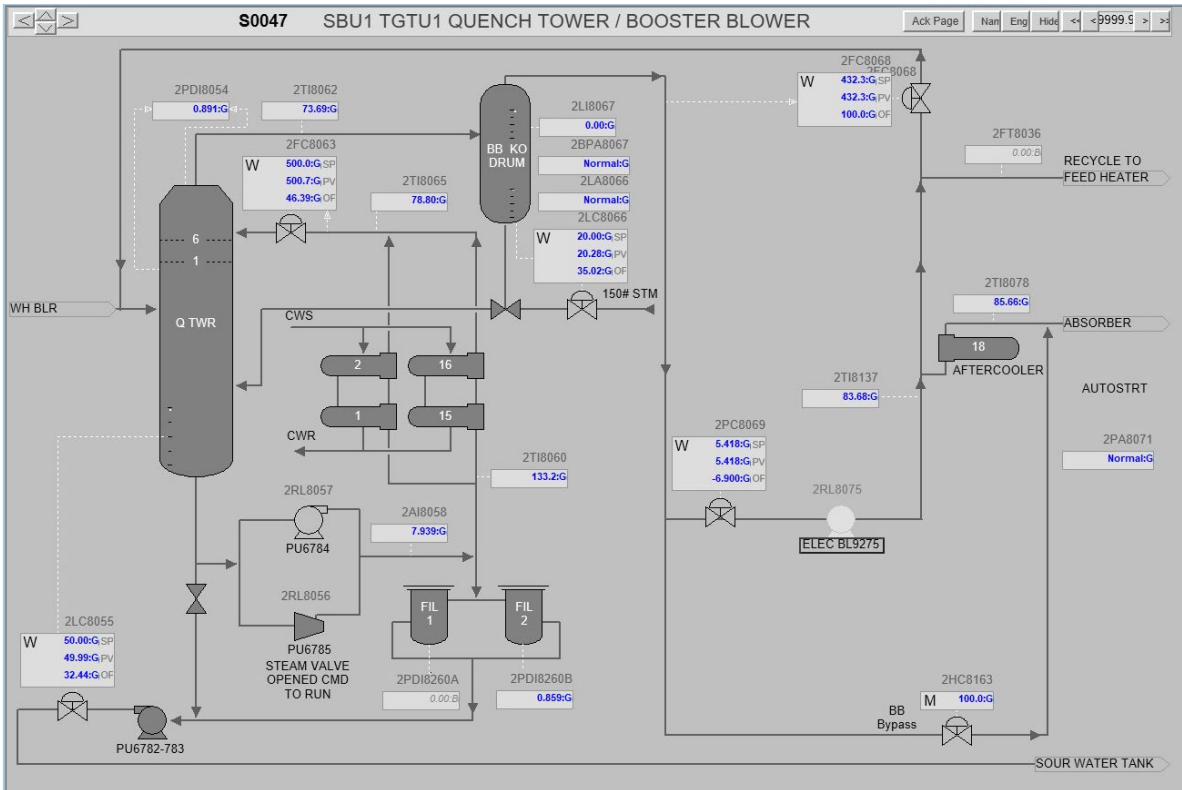
The first attempt observed a very strong exotherm which immediately required halting sulfiding to cool the Reactor, regroup, and start with a lower RIT. The first controlled test of this procedure started with RIT <300°F, introduction of Sulfiding H₂S, ramp-up of RIT to ~440°F, and then introduction of H₂. The observed exotherm was very strong requiring sulfiding to be stopped and cooling of the reactor.

After seeing the strong exotherm that could be obtained, the decision was made by the Team to add both H₂S and H₂ while at low RIT and then slowly ramp the RIT to observe the desired Reactor Bed Temperatures, which proved very successful. Reduction of H₂ and/or H₂S flows would be used to control the exotherm. During the first attempt, the Team proved that the exotherm could be quickly controlled by adjusting the H₂S and H₂.

TGTU1 Steam Heat Exchanger, Hot Oil Heat Exchanger, Reactor, and Waste Heat Boiler



TGTU1 Quench Tower





Sulfiding Low Temperature TGTU Catalyst - Timeline

- Nov 4th
 - 7:00 PM RIT ~165°F, SRU in Natural Gas sweep Tail Gas through TGTU, Sulfiding AG 10MSFCH
 - 8:30 PM Sulfiding AG increased to 15 MSCFH
 - 9:00 PM TGTU AG Recycle increase observed and Absorber H2S observed
- Nov 5th
 - 02:00 AM H2 Introduced at 5 MSCFH
 - 03:30 AM RIT slow ramp-up initiated from ~165°F, increased Sulfiding AG to 15 MSCFH
 - 05:45 AM RIT 275°F, 10% Bed Exotherm observed
 - 06:30 AM RIT 282°F, strong 10% Bed exotherm, reduced Sulfiding AG to 10.5 MSCFH
 - 07:00 AM RIT 288°F, 10%/50% Bed exotherms
 - 07:35 AM RIT 290°F, 10%/50% Bed exotherms, reduced Sulfiding AG to 8.5 MSCFH
 - 08:30 AM RIT 300°F, 10%/50%/75% Bed exotherms, increased H2 to 8 MSCF with observed H2 reduction
 - 09:30 AM RIT 308°F, 10%/50%/75% Bed strong exotherms, reduced Sulfiding AG to 5.8 MSCFH and H2 to 3.5 MSCFH
 - 10:30 AM RIT 313°F, 10%/50%/75%/ROT Bed exotherms, maintained Sulfiding AG at 5.8 MSCFH and reduced H2 to 0.0 MSCFH
 - 11:15 AM 10% Bed Exotherm peaked and turned
 - 11:30 AM RIT 310°F, re-introduced H2 at 1.8 MSCFH and slowly ramped up to 5.0 MSCFH
 - 8:30 PM SRU2 AAG introduction, reduced Sulfiding AG
 - 11:55 PM SRU3 AAG introduction

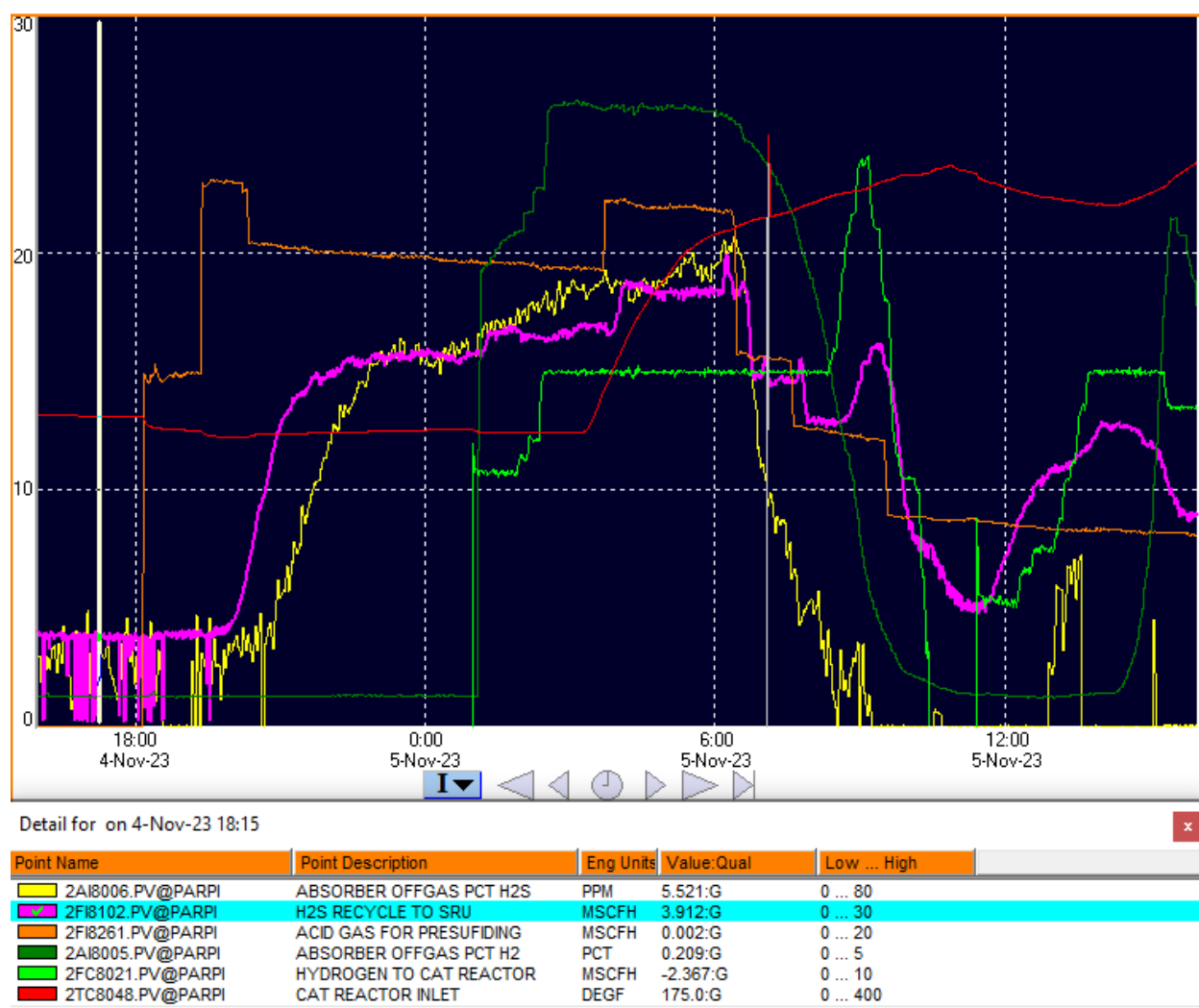
Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 4th

6:15 PM, RIT ~175°F,

SRU in Natural Gas sweep

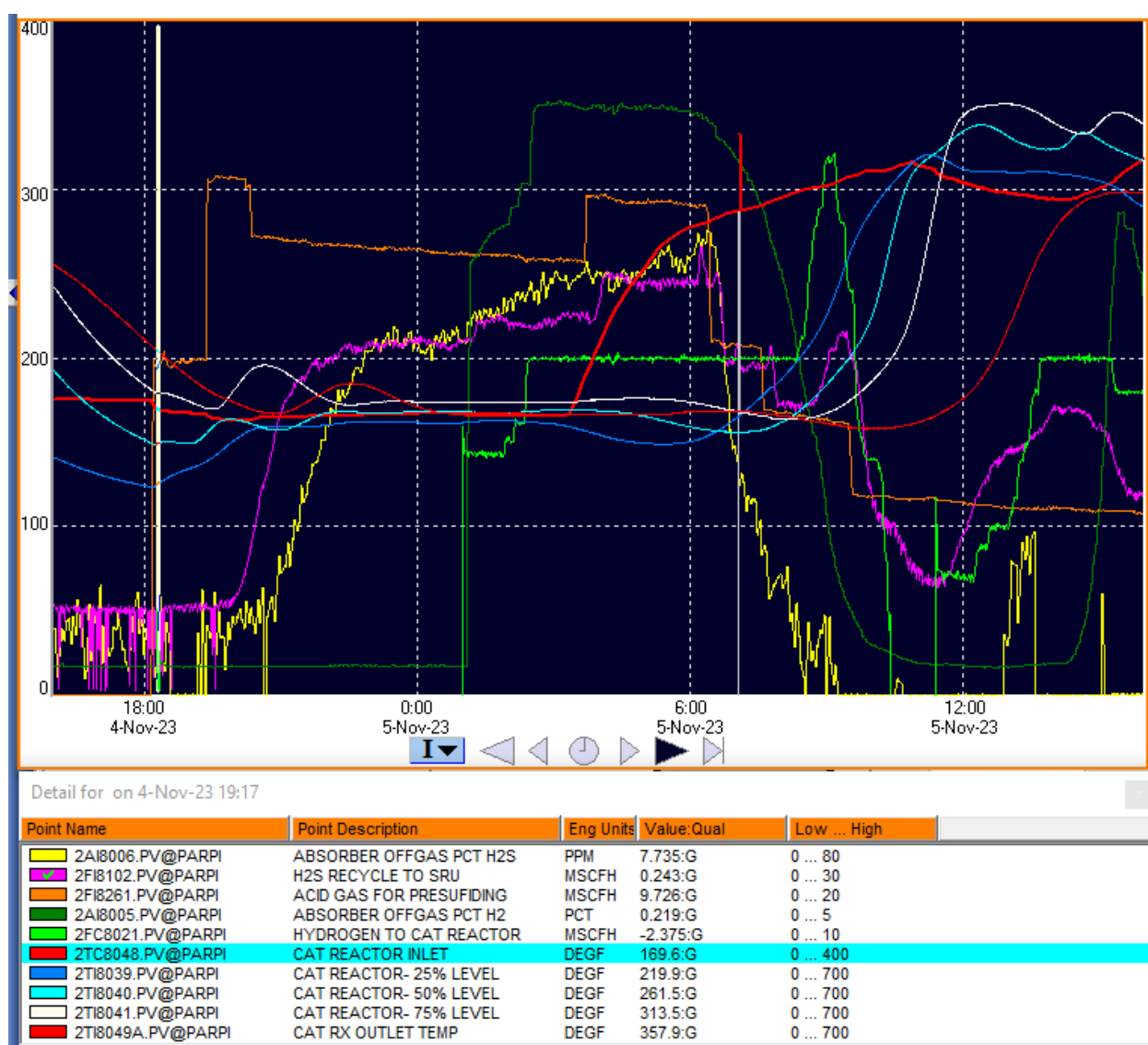
Tail Gas through TGTU1



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 4th

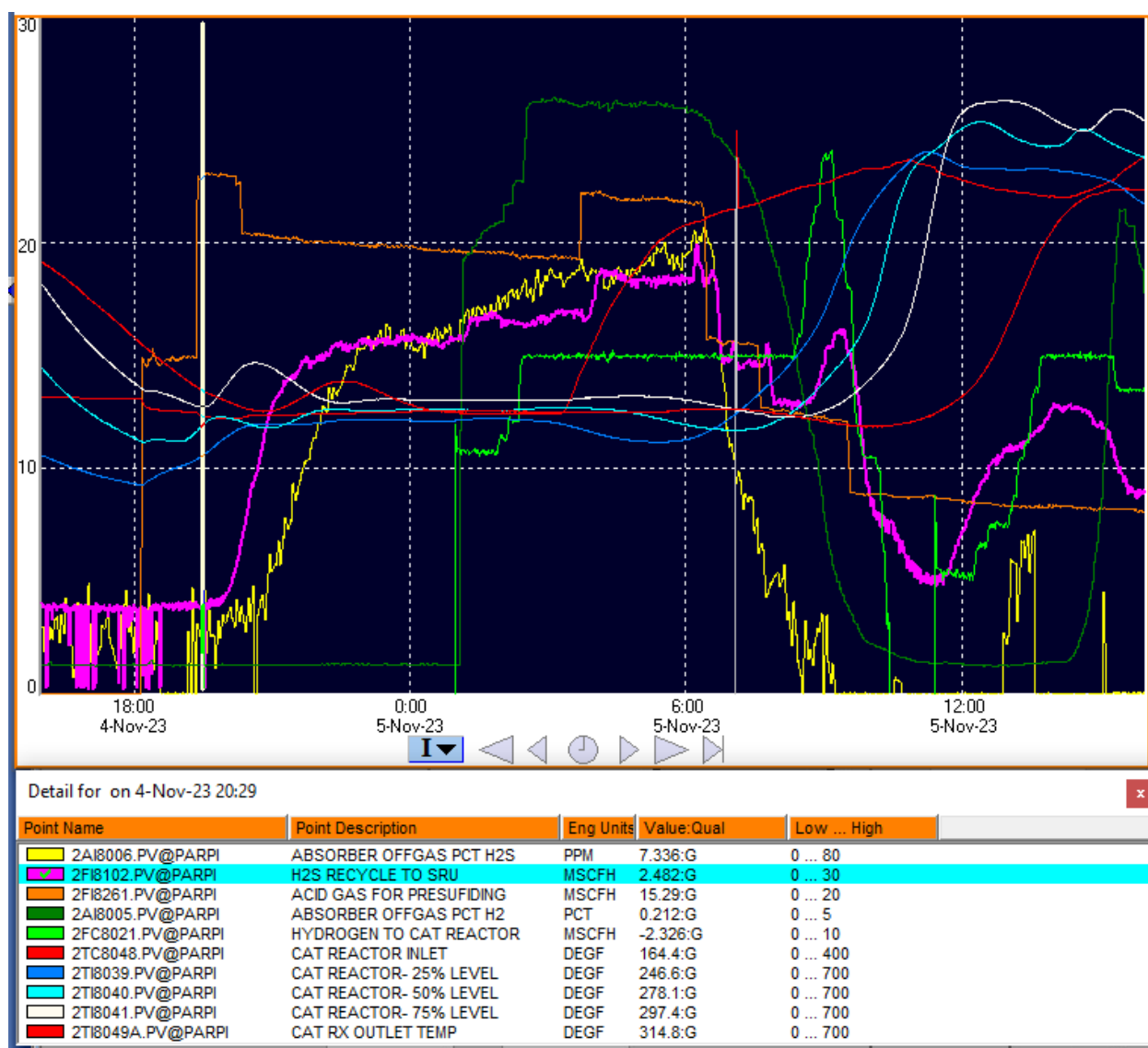
7:00 PM, Sulfiding AG 10 MSCFH



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 4th

8:30 PM, Sulfiding AG increased to 15 MSCFH



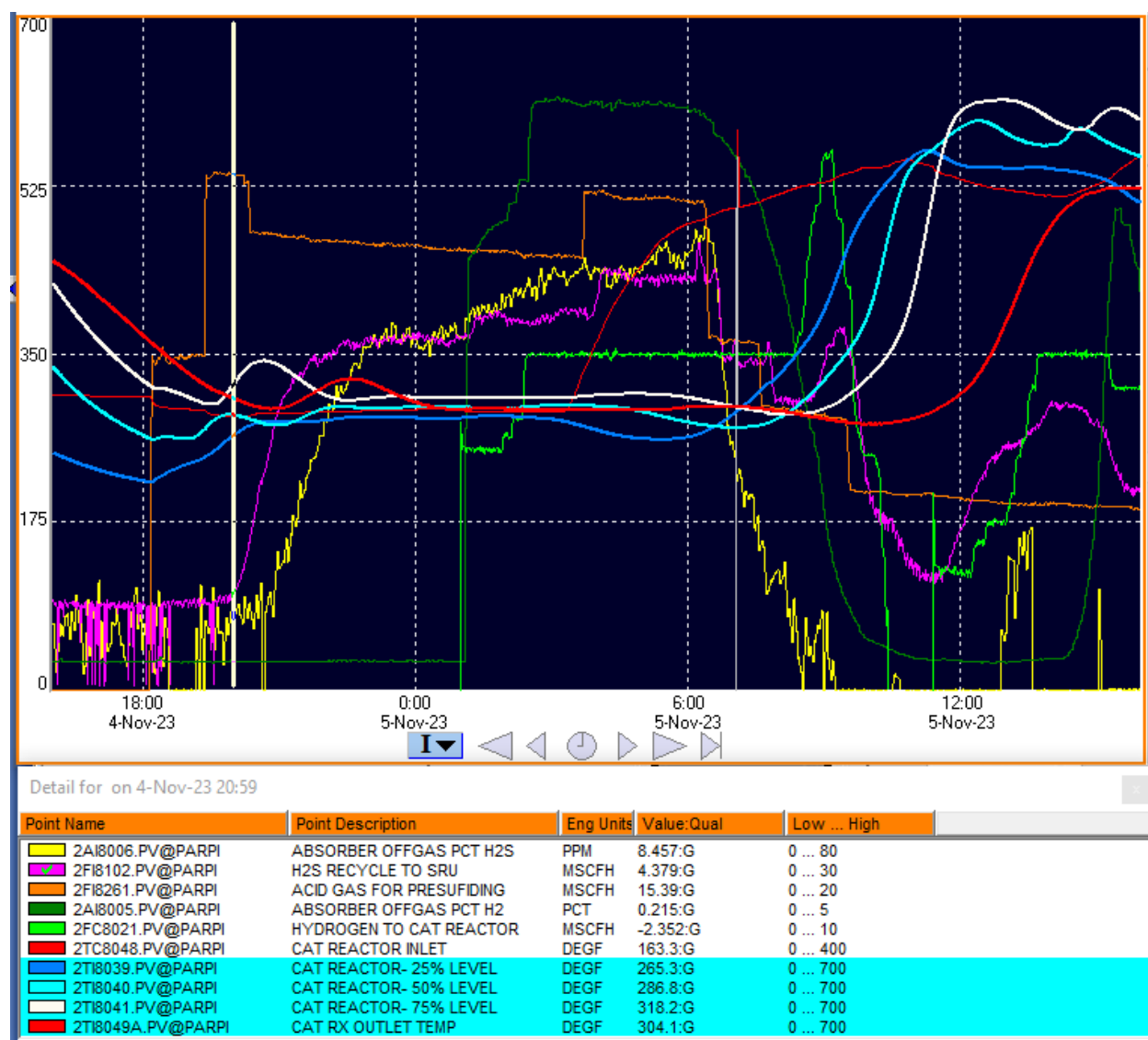
Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 4th

9:00 PM

TGTU AG Recycle increase observed

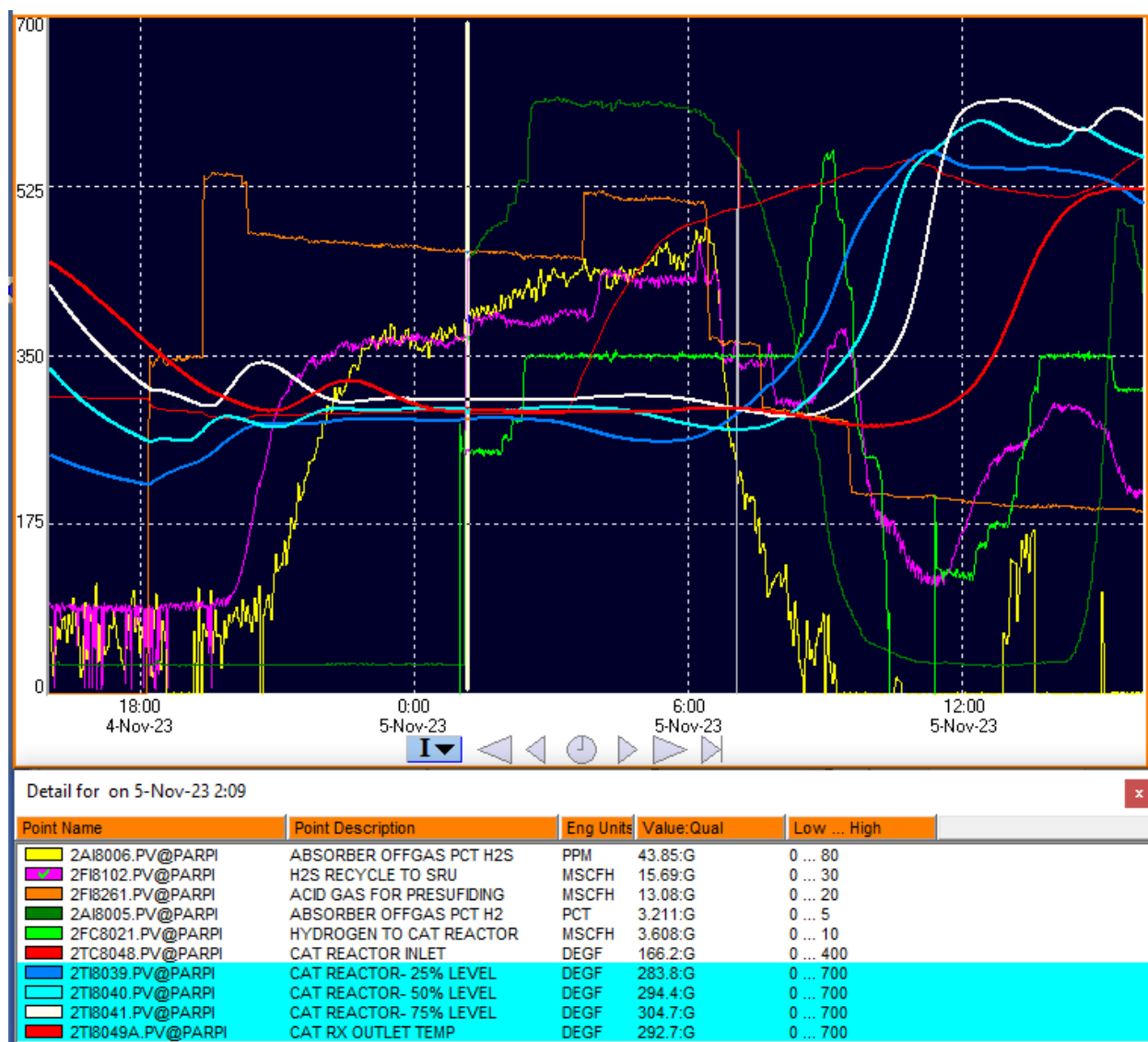
Absorber OH H2S observed



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

02:00 AM, H2 Introduced at 5 MSCFH



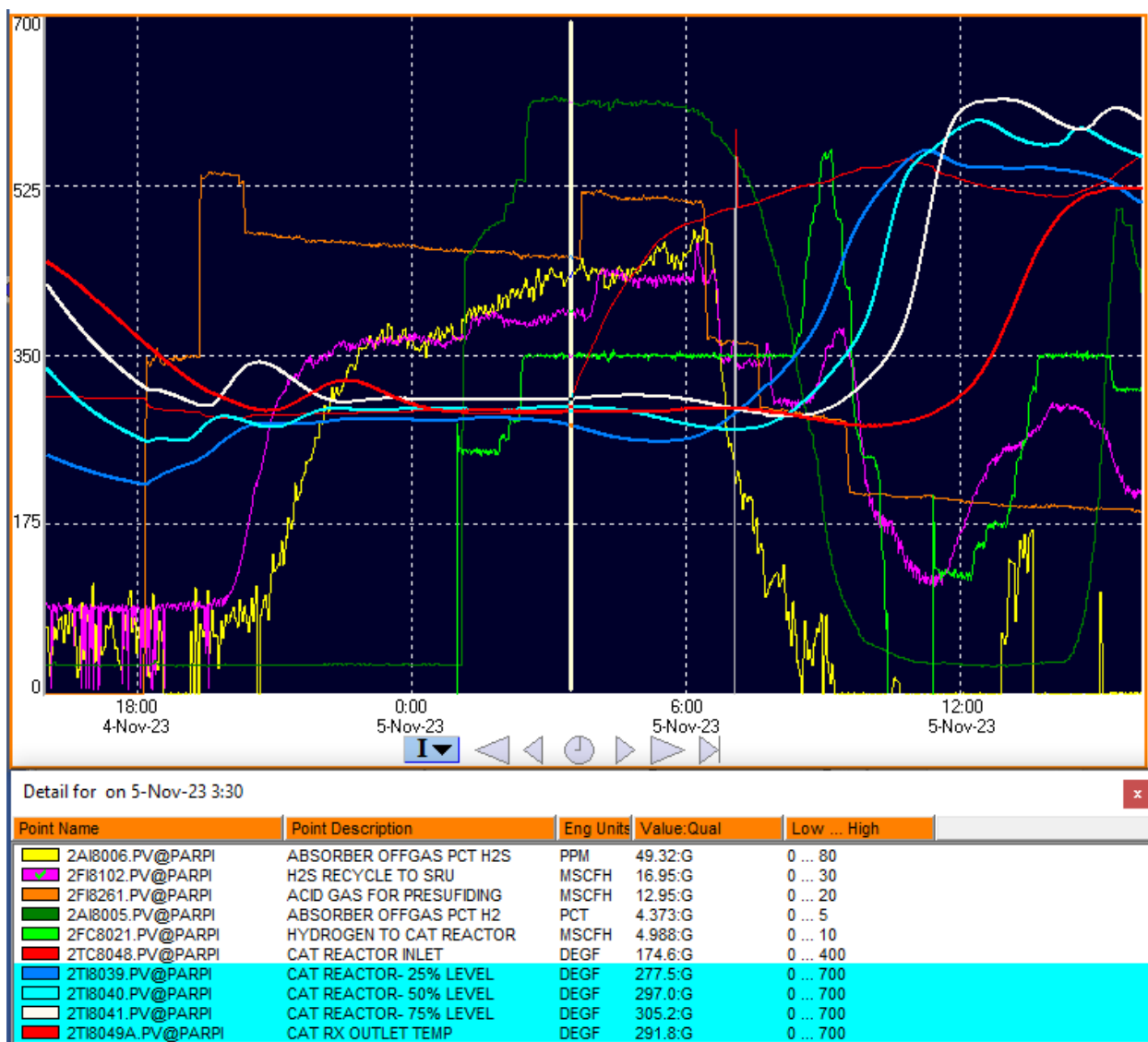
Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

03:30 AM

RIT slow ramp-up initiated from ~165°F

Sulfiding AG increased to 15 MSCFH



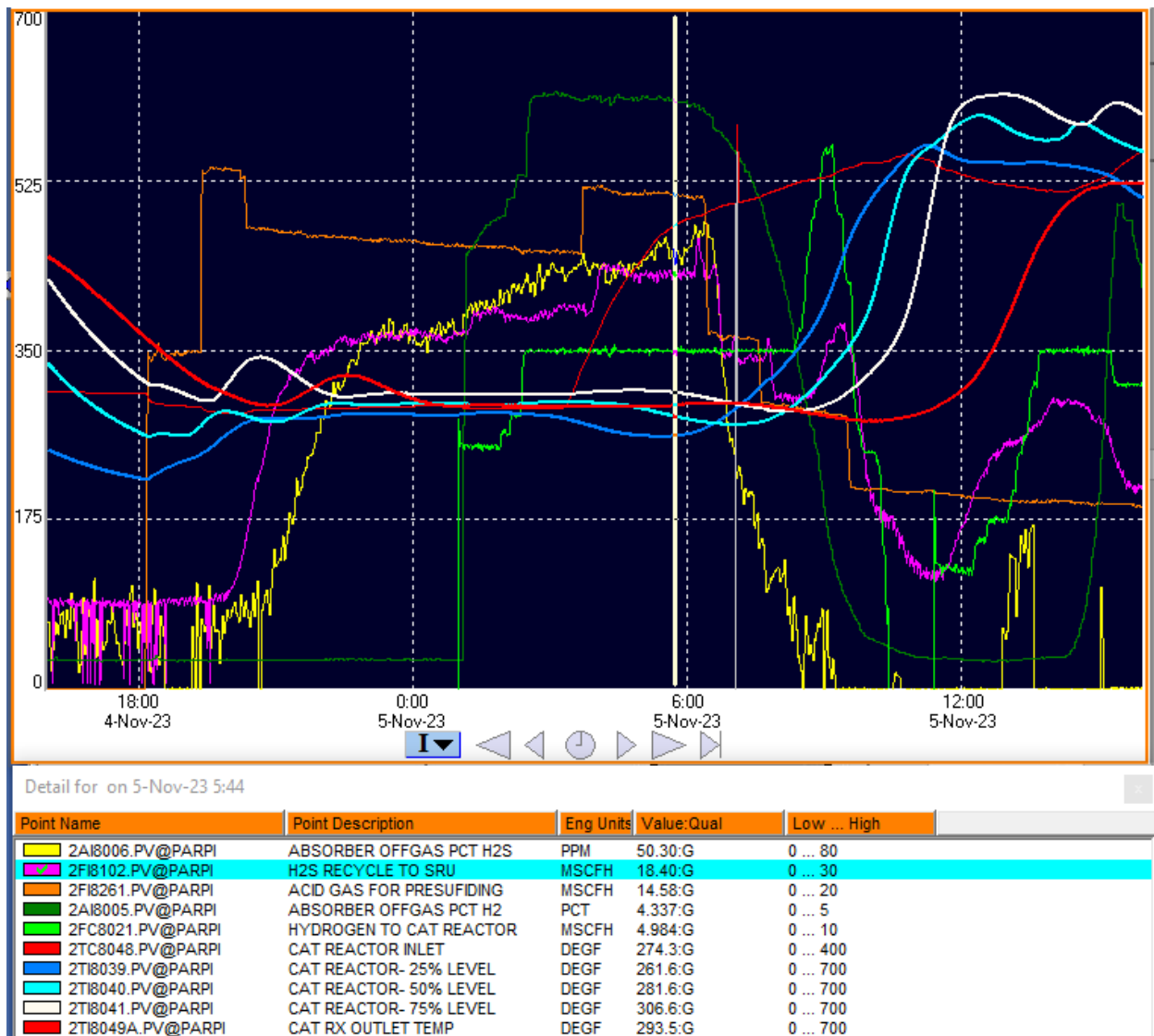
Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

05:45 AM

RIT 275°F

10% Bed Exotherm observed



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

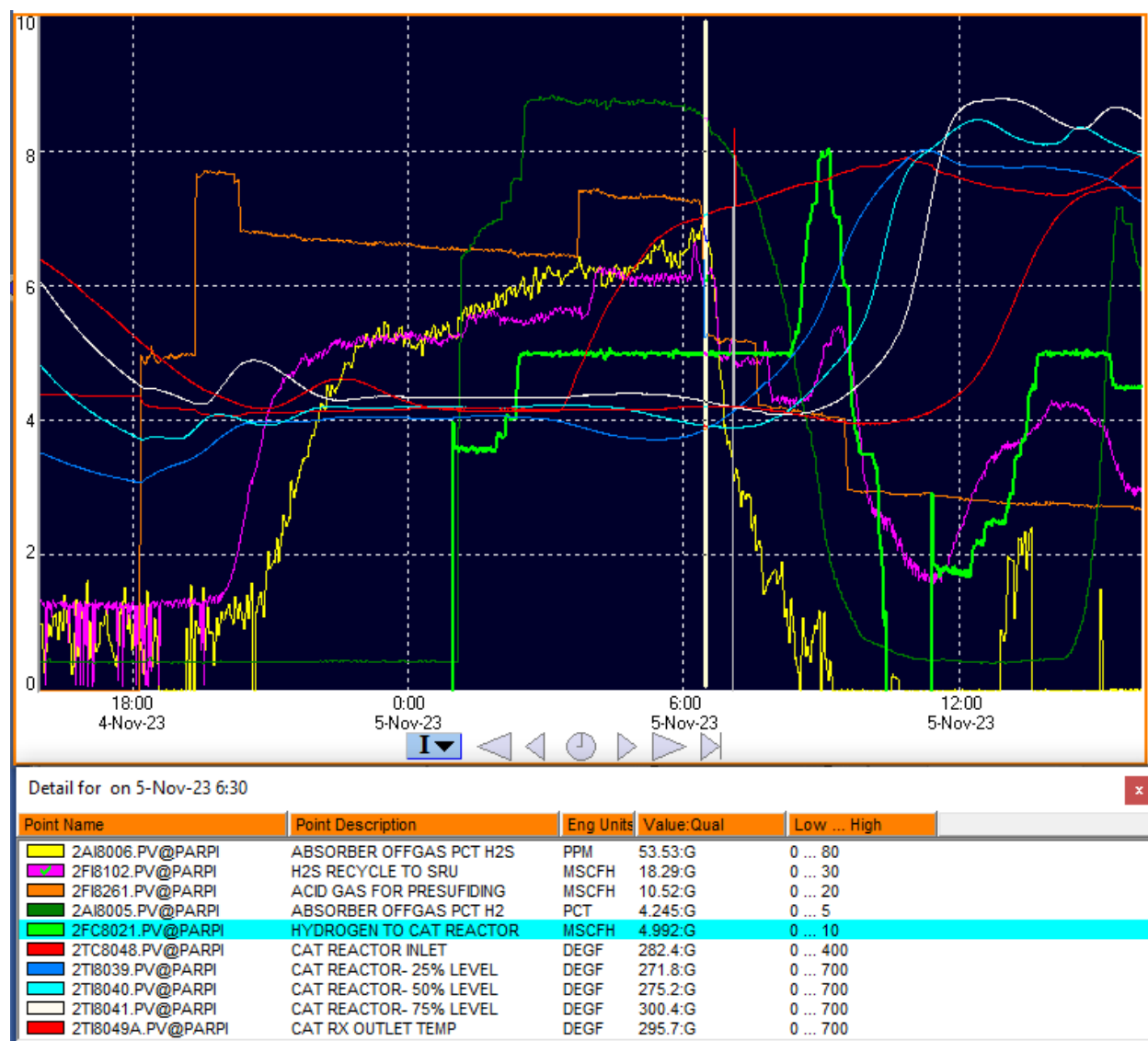
Nov 5th

06:30 AM

RIT 282°F

Strong 10% Bed exotherm starting

Reduced Sulfiding AG to 10.5 MSCFH



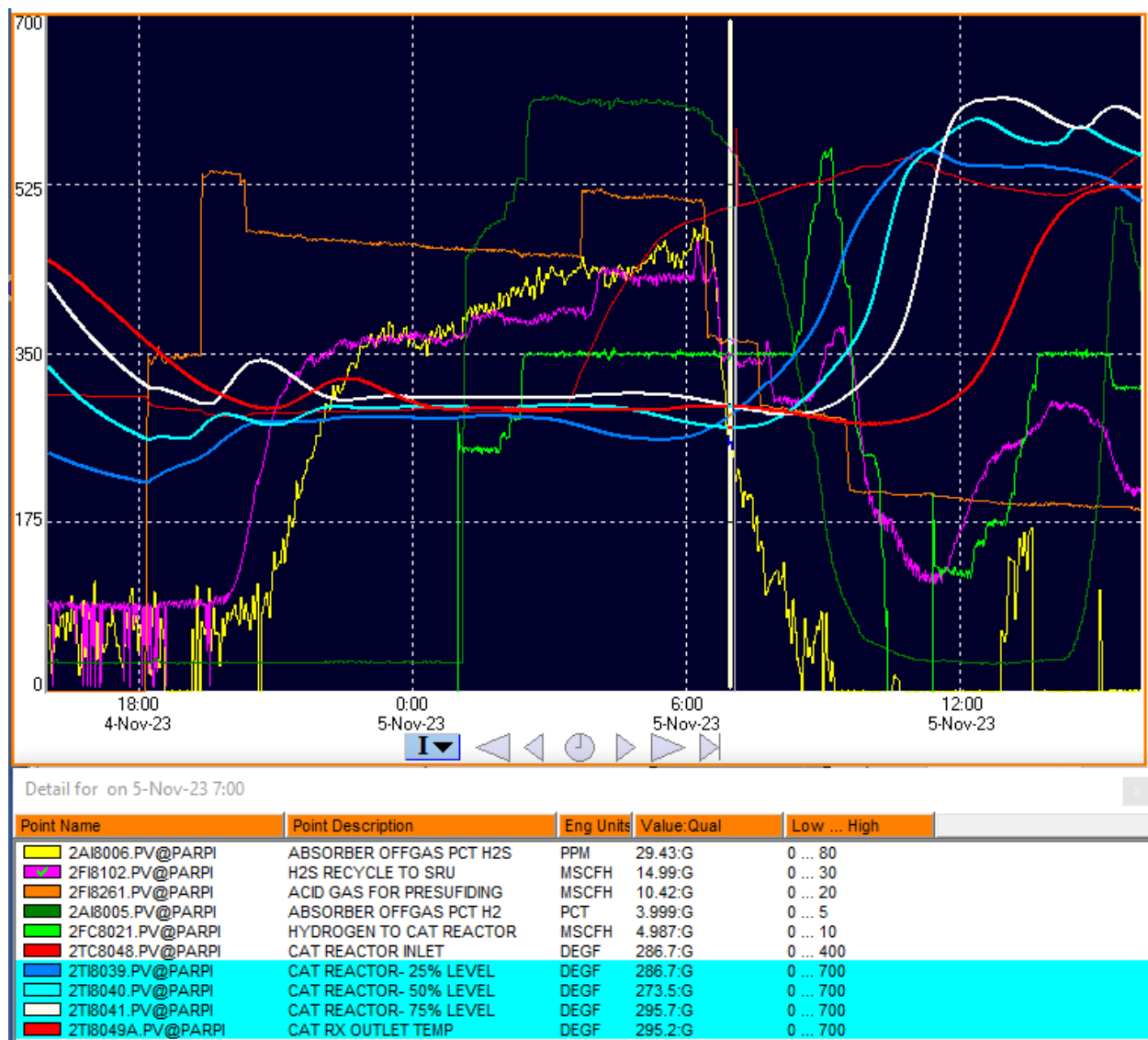
Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

07:00 AM

RIT 288°F

10%/50% Bed exotherms



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

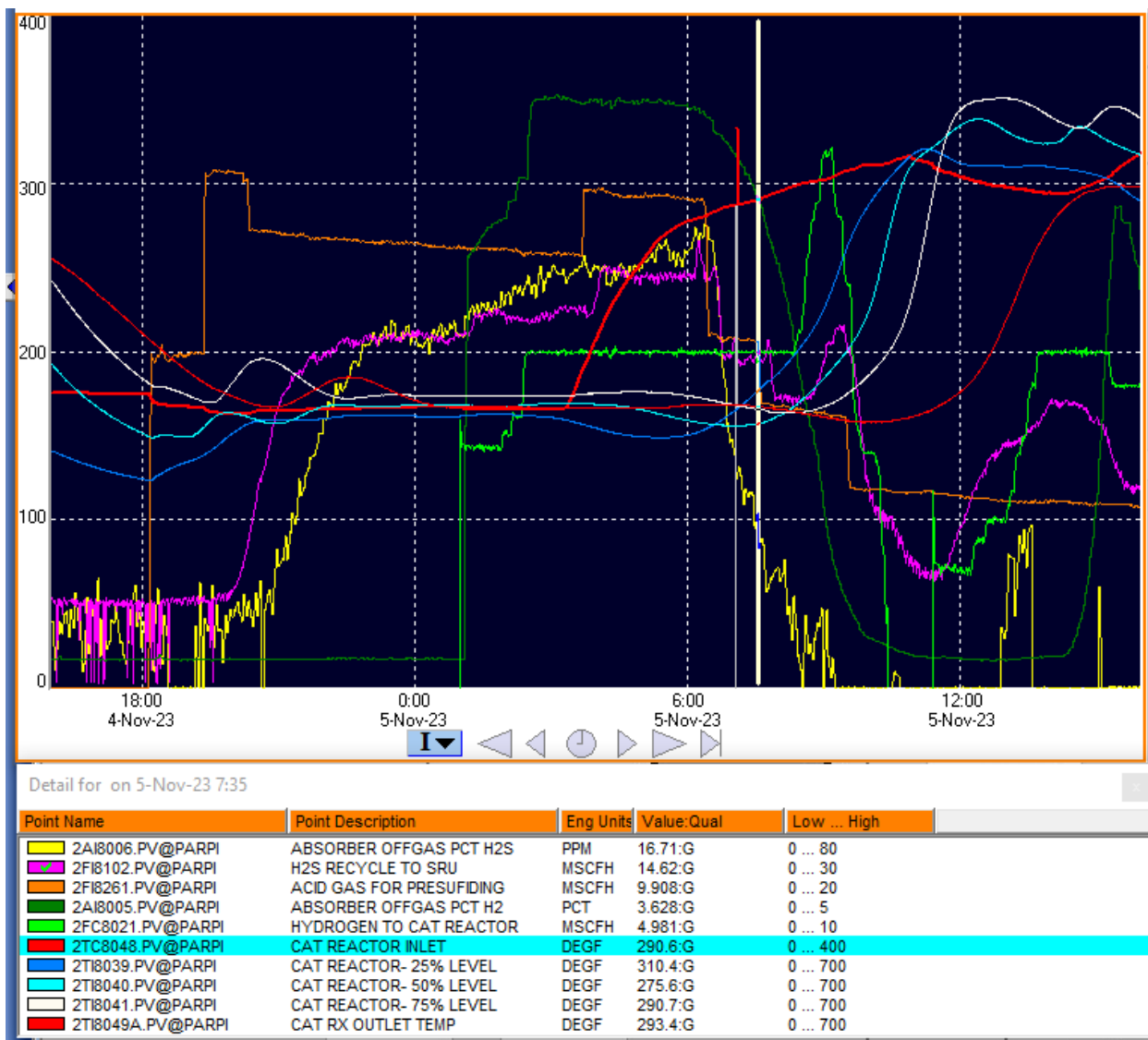
Nov 5th

07:35 AM

RIT 290°F

10%/50% Bed exotherms

Reduced Sulfiding AG to 8.5 MSCFH



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

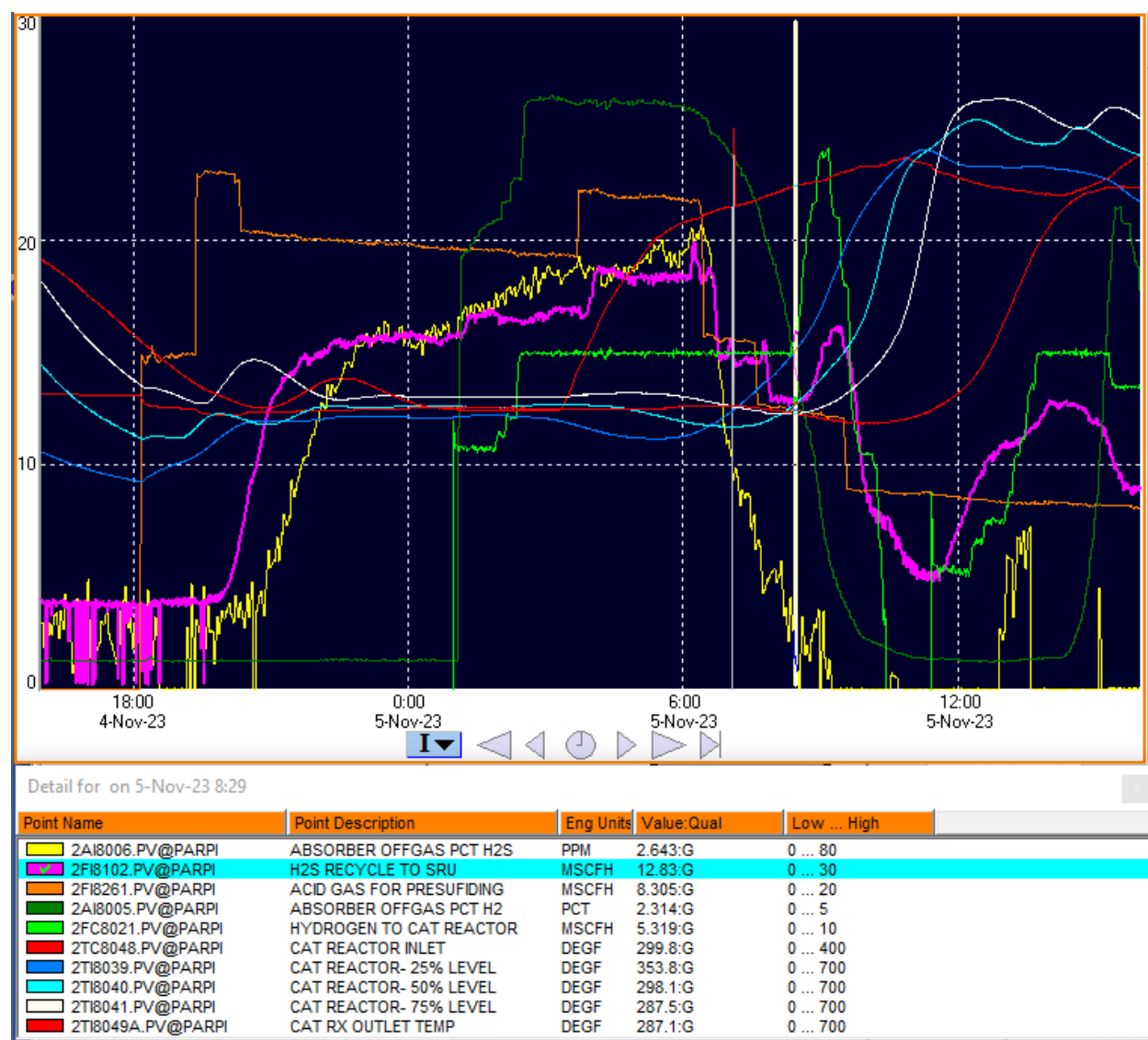
08:30 AM

RIT 300°F

10%/50%/75% Bed exotherms

Observe H2 concentration reduction at Absorber OH

Increased H2 to 8 MSCF



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

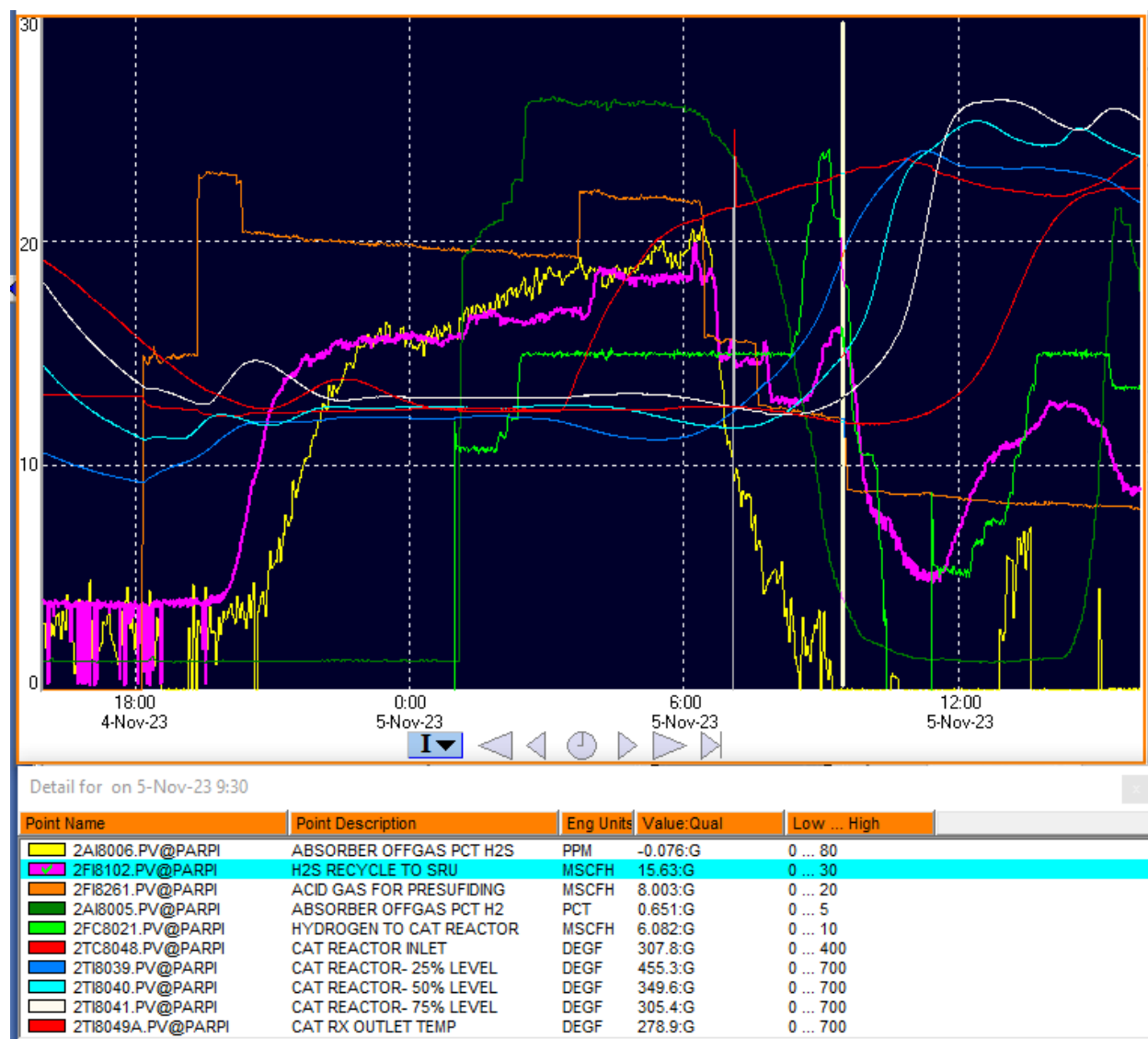
09:30 AM

RIT 308°F

10%/50%/75% **STRONG** Bed exotherms

Reduced Sulfiding AG to 5.8 MSCFH

Reduced H2 to 3.5 MSCFH



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

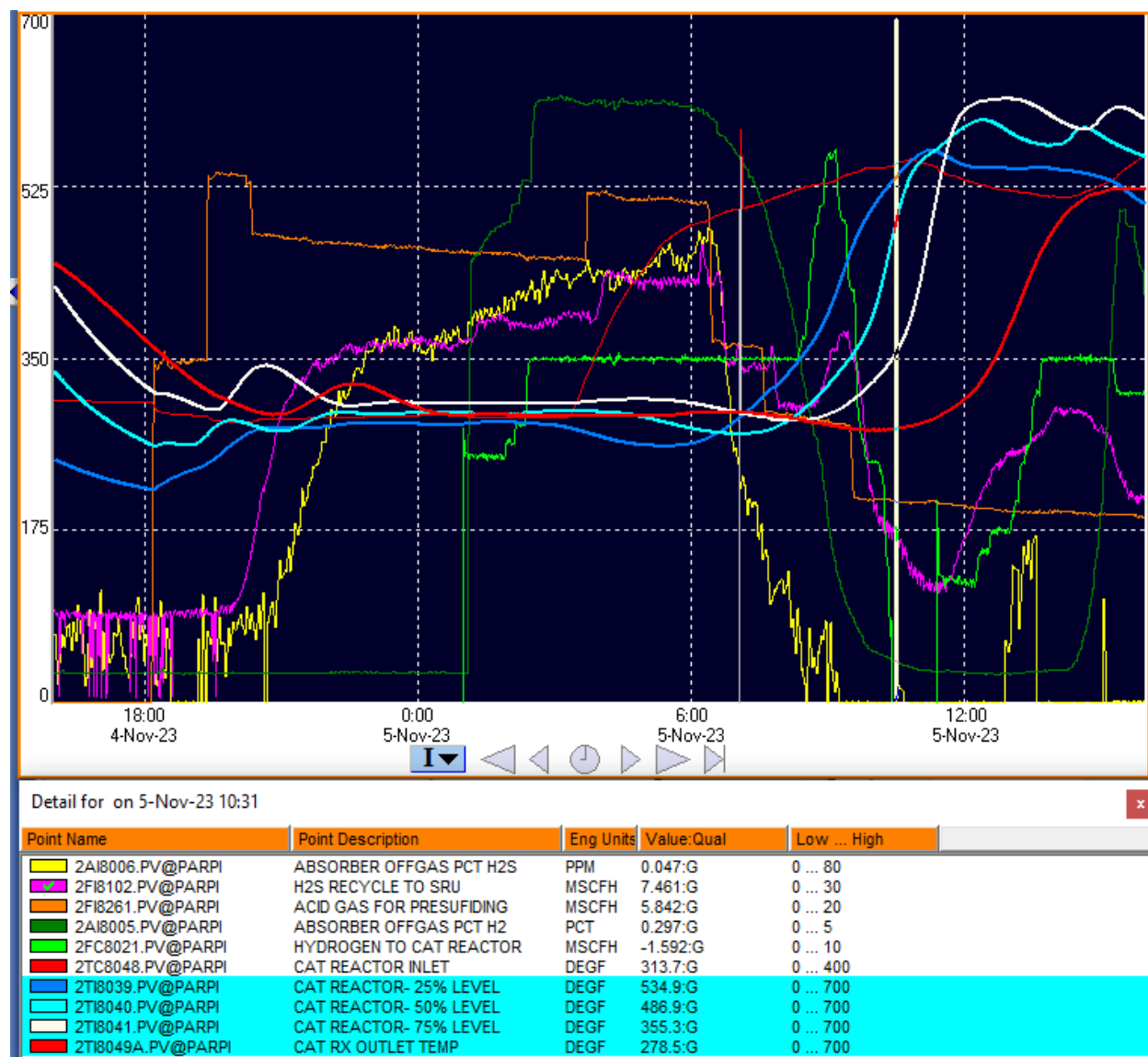
10:30 AM

RIT 313°F

10%/50%/75%/ROT **STRONG** Bed exotherms

Maintained Sulfiding AG at 5.8 MSCFH

Reduced H2 to 0.0 MSCFH to turn the exotherm



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

11:15 AM

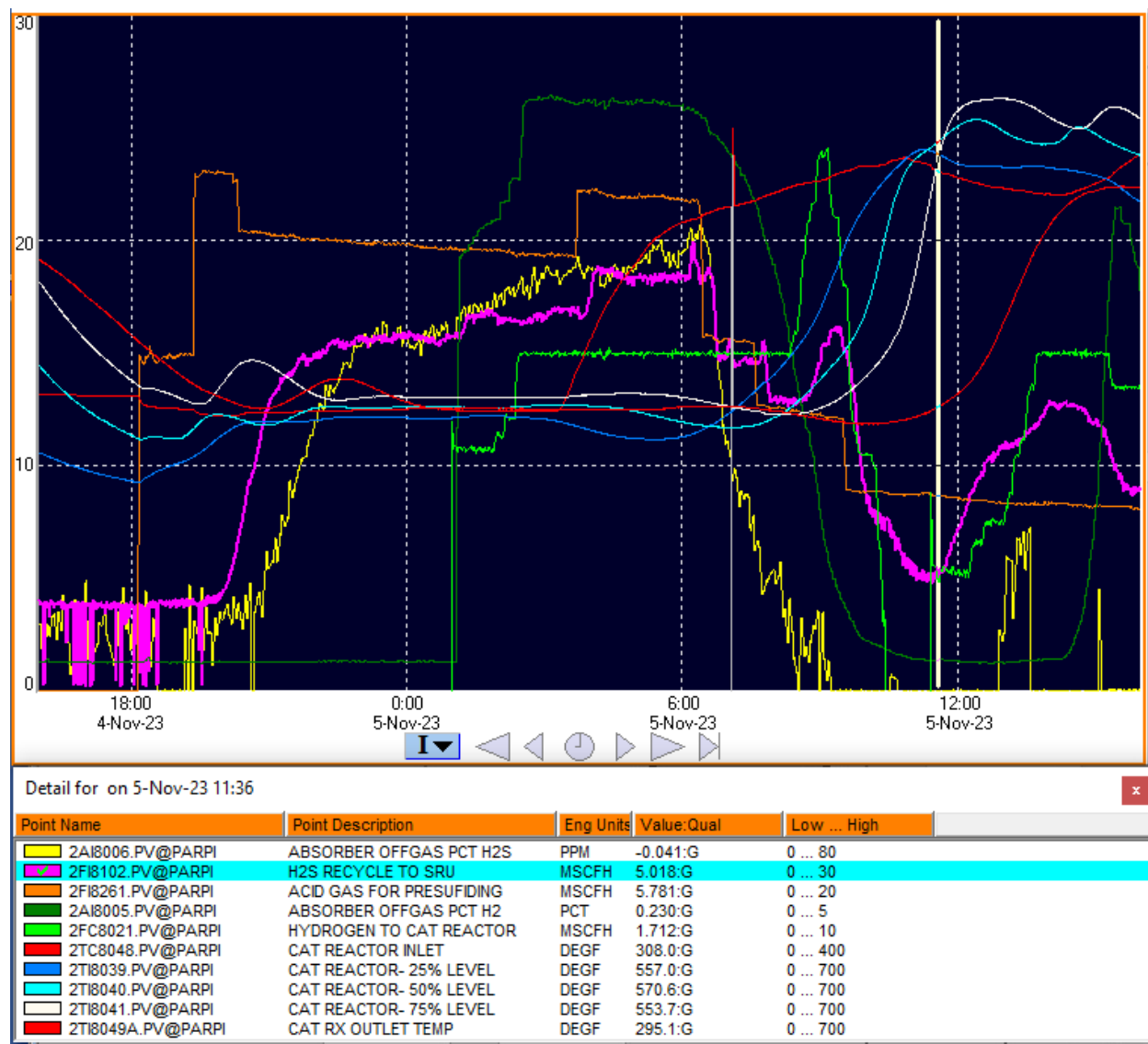
10% Bed Exotherm **peaked and turned**

11:30 AM

RIT 310°F

Re-introduced H2 at 1.8 MSCFH

Slowly ramped H2 up to 5.0 MSCFH



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

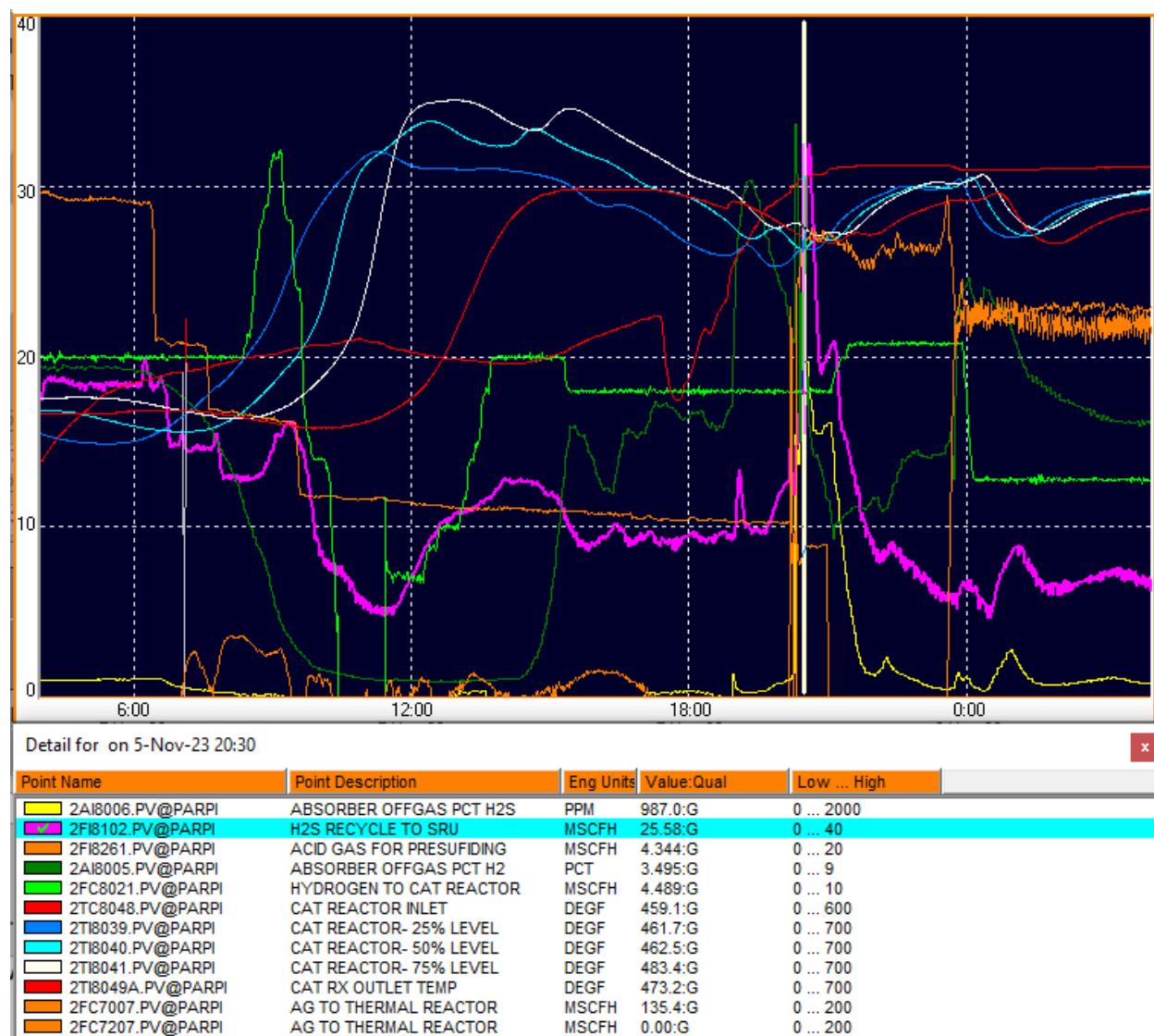
20:30 (8:30 PM)

SRU2 AAG introduction

Reduced Sulfiding AG

21:00 (9:00 PM)

Stopped Sulfiding AG

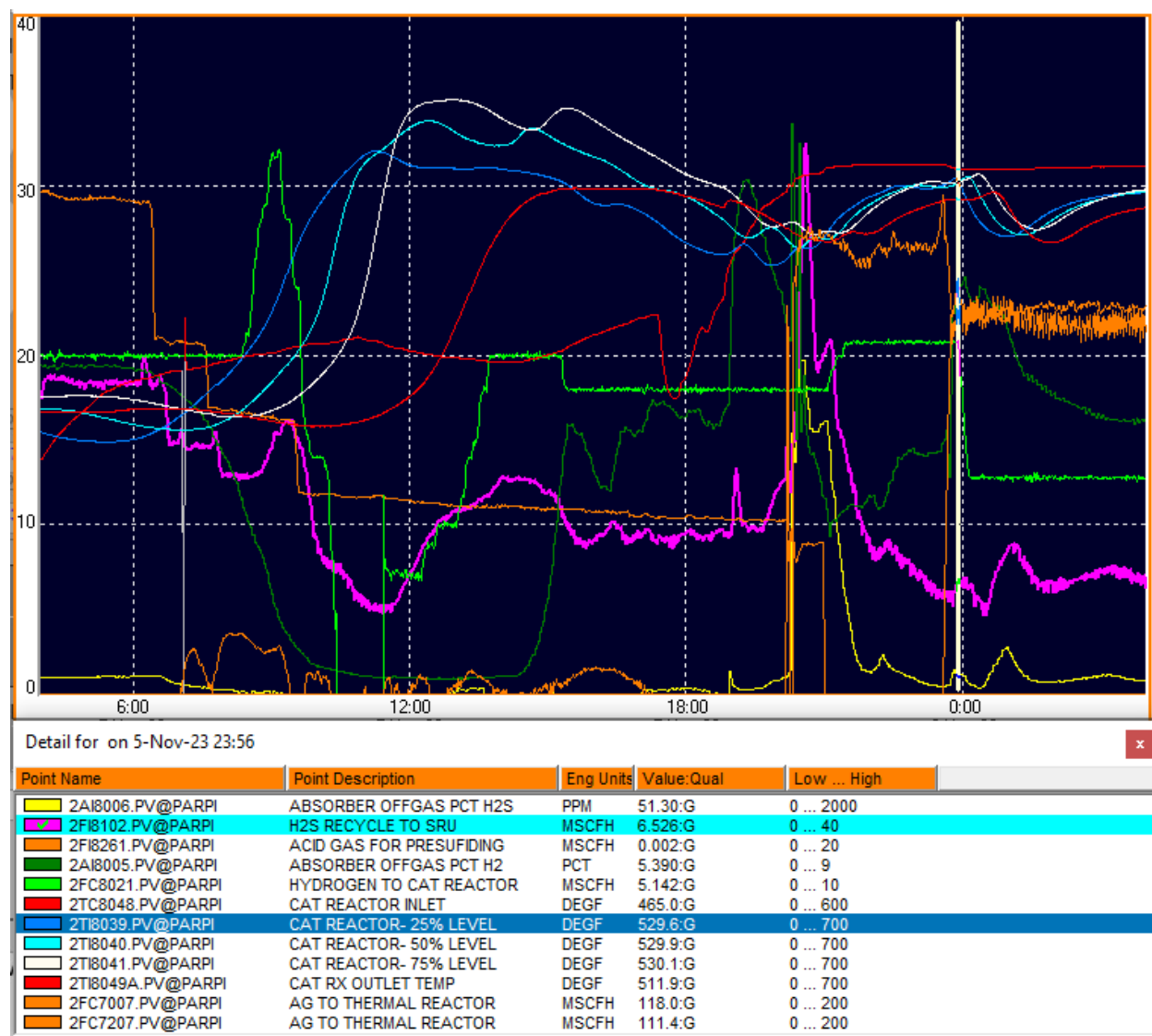


Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

Nov 5th

23:55 (11:55 PM)

SRU3 AAG introduction



Sulfiding Low Temperature TGTU Catalyst - Timeline (continued)

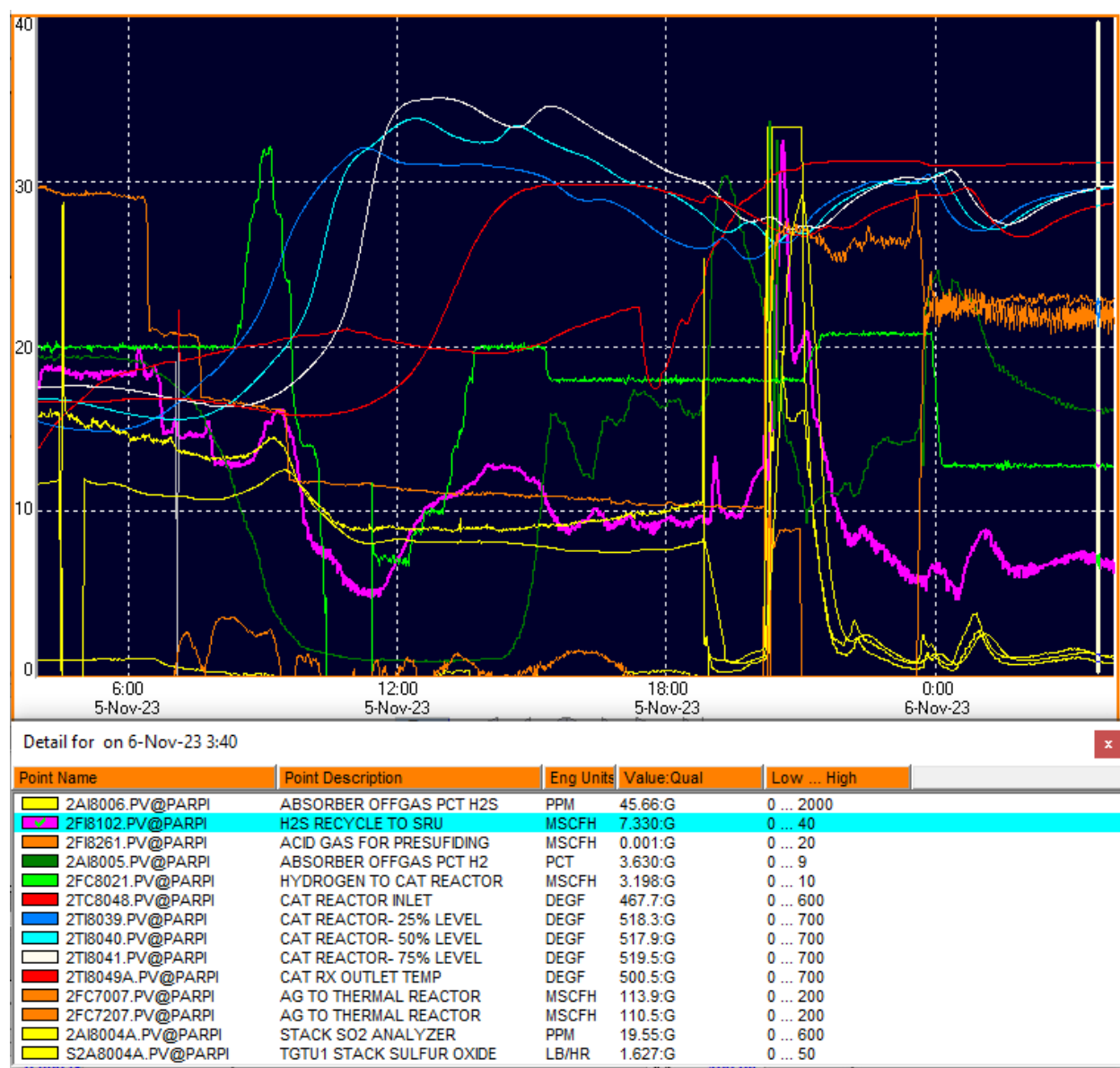
Nov 6th

03:40 AM

Incinerator Emissions within Environmental Limits

~20 ppm

1.5 lb/hr SO₂



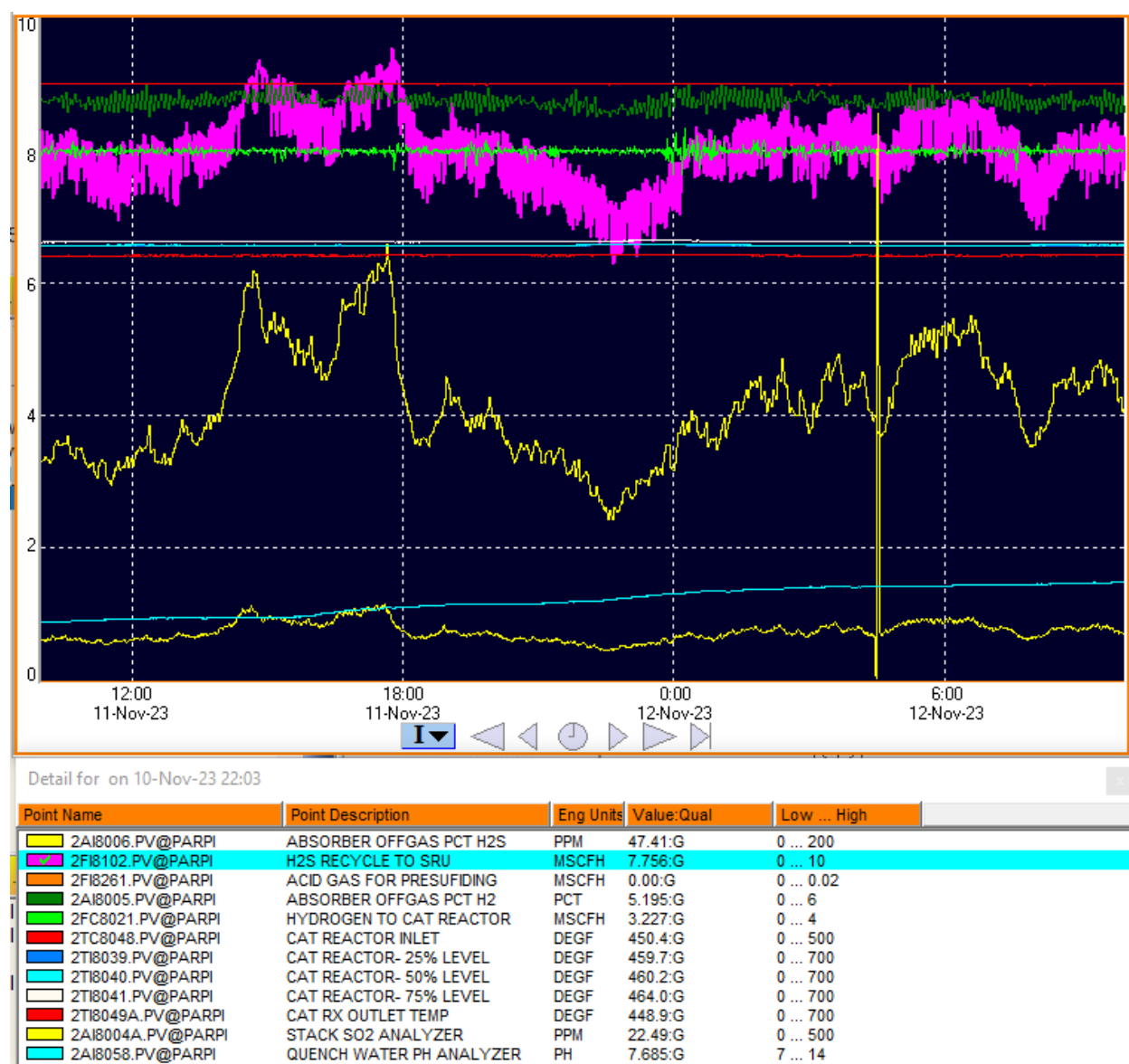
Sulfiding Low Temperature TGTU Catalyst – Timeline (continued)

Nov 10th

22:00 (10:00 PM)

Operating well

pH added to trend



Sulfiding Low Temperature TGTU Catalyst – Lessons Learned

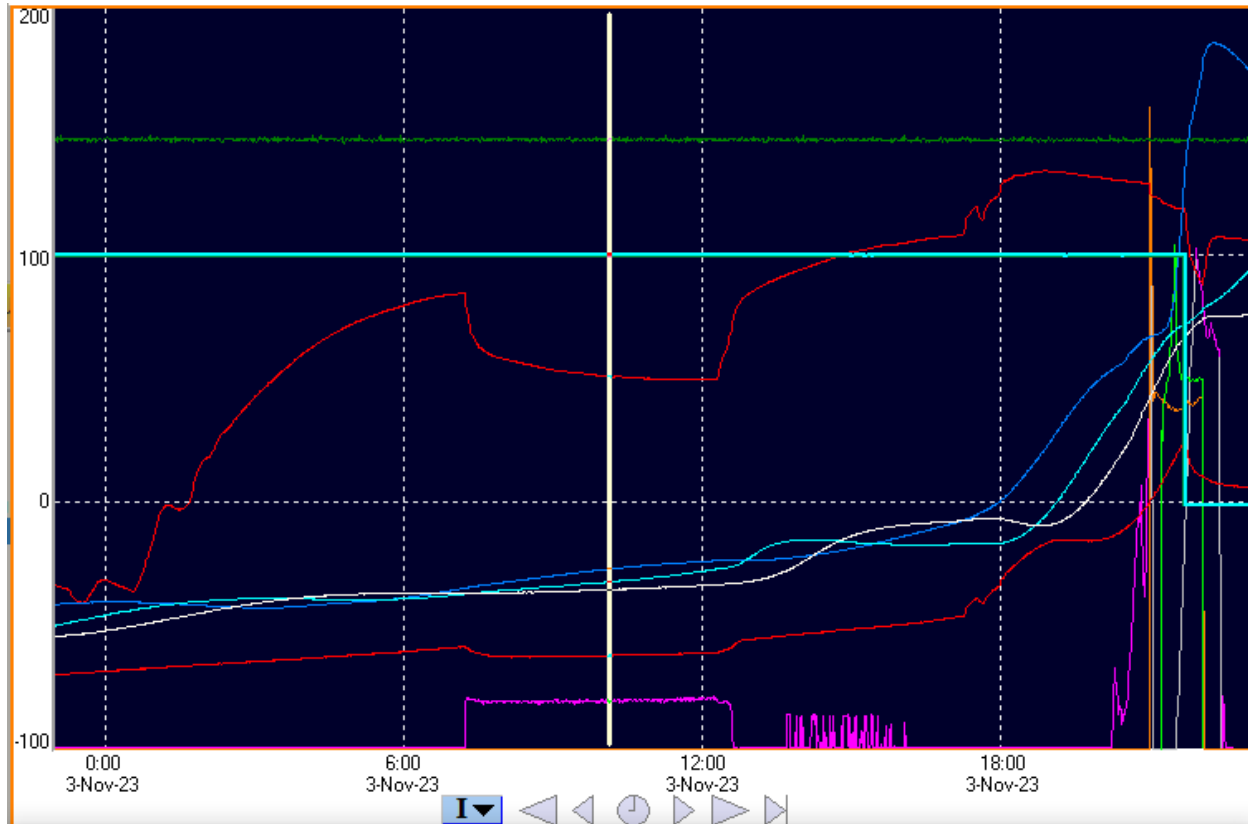
- The first attempt observed a very strong exotherm which immediately required halting sulfiding to cool the Reactor, regroup, and start with a lower RIT.
- The first controlled test of this procedure started with RIT <300°F, introduction of Sulfiding H₂S, ramp-up of RIT to ~440°F, and then introduction of H₂.
- The observed exotherm was very strong requiring sulfiding to be stopped and cooling of the reactor.
- After seeing the strong exotherm that could be obtained, the decision was to add both H₂S and H₂ while at low RIT and then slowly ramp the RIT to observe the desired Reactor Bed Temperatures, which proved very successful.
- We also proved that the exotherm could be quickly controlled by adjusting the H₂S and H₂.

Sulfiding Low Temperature TGTU Catalyst – 1st Attempt Timeline

Nov 3rd

RIT slow ramp up

Small flow Sulfiding AG



Detail for on 3-Nov-23 10:09

| Point Name | Point Description | Eng Units | Value:Qual | Low ... High |
|-------------------|---------------------------|-----------|------------|--------------|
| 2AI8006.PV@PARPI | ABSORBER OFFGAS PCT H2S | PPM | 10.31:G | -10 ... 0 |
| 2FI8102.PV@PARPI | H2S RECYCLE TO SRU | MSCFH | 5.269:G | 0 ... 80 |
| 2FI8261.PV@PARPI | ACID GAS FOR PRESULFIDING | MSCFH | 0.00:G | 0 ... 20 |
| 2AI8005.PV@PARPI | ABSORBER OFFGAS PCT H2 | PCT | 0.412:G | 0 ... 0.5 |
| 2FC8021.PV@PARPI | HYDROGEN TO CAT REACTOR | MSCFH | -2.491:G | 0 ... 8 |
| 2TC8048.PV@PARPI | CAT REACTOR INLET | DEGF | 302.0:G | 0 ... 600 |
| 2TI8039.PV@PARPI | CAT REACTOR- 25% LEVEL | DEGF | 207.1:G | 0 ... 850 |
| 2TI8040.PV@PARPI | CAT REACTOR- 50% LEVEL | DEGF | 192.3:G | 0 ... 850 |
| 2TI8041.PV@PARPI | CAT REACTOR- 75% LEVEL | DEGF | 183.1:G | 0 ... 850 |
| 2TI8049A.PV@PARPI | CAT RX OUTLET TEMP | DEGF | 107.7:G | 0 ... 850 |
| 2ZI8000.PV@PARPI | SRU2 GAS TO TGTU1 FD HTR | PCT | 99.95:G | -100 ... 200 |
| 2ZI8002.PV@PARPI | SRU3 TO TGTU1 DV POSITN | PCT | 100.2:G | -100 ... 200 |

Sulfiding Low Temperature TGTU Catalyst – 1st Attempt Timeline

Nov 3rd

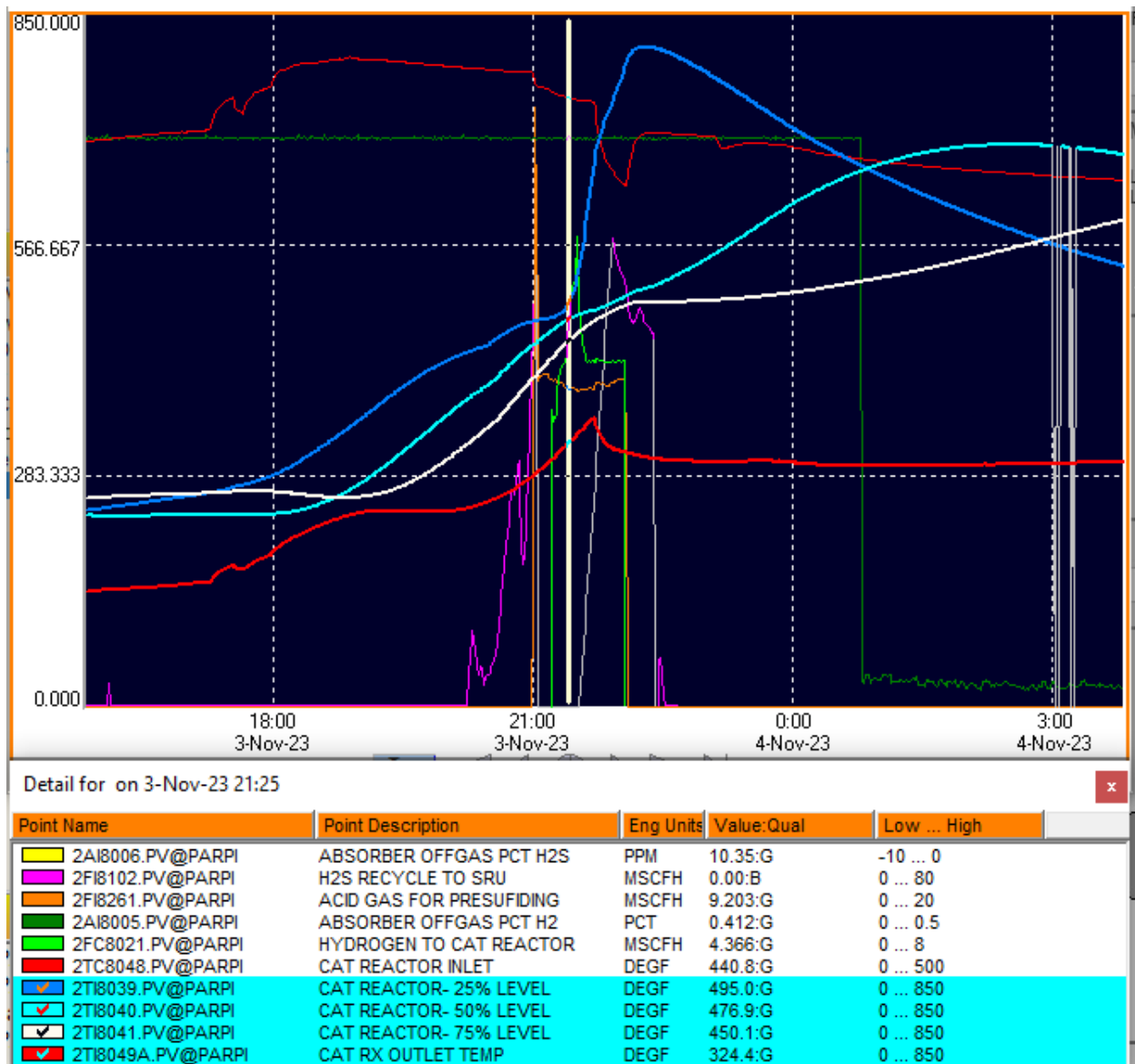
21:25 (9:25 PM)

RIT ~340°F

Sulfiding AG increased

H2 introduced

Very strong 10% Bed exotherm starting to be observed



Sulfiding Low Temperature TGTU Catalyst – 1st Attempt Timeline

Nov 3rd

22:00 (10:00 PM)

Very strong 10% Bed exotherm

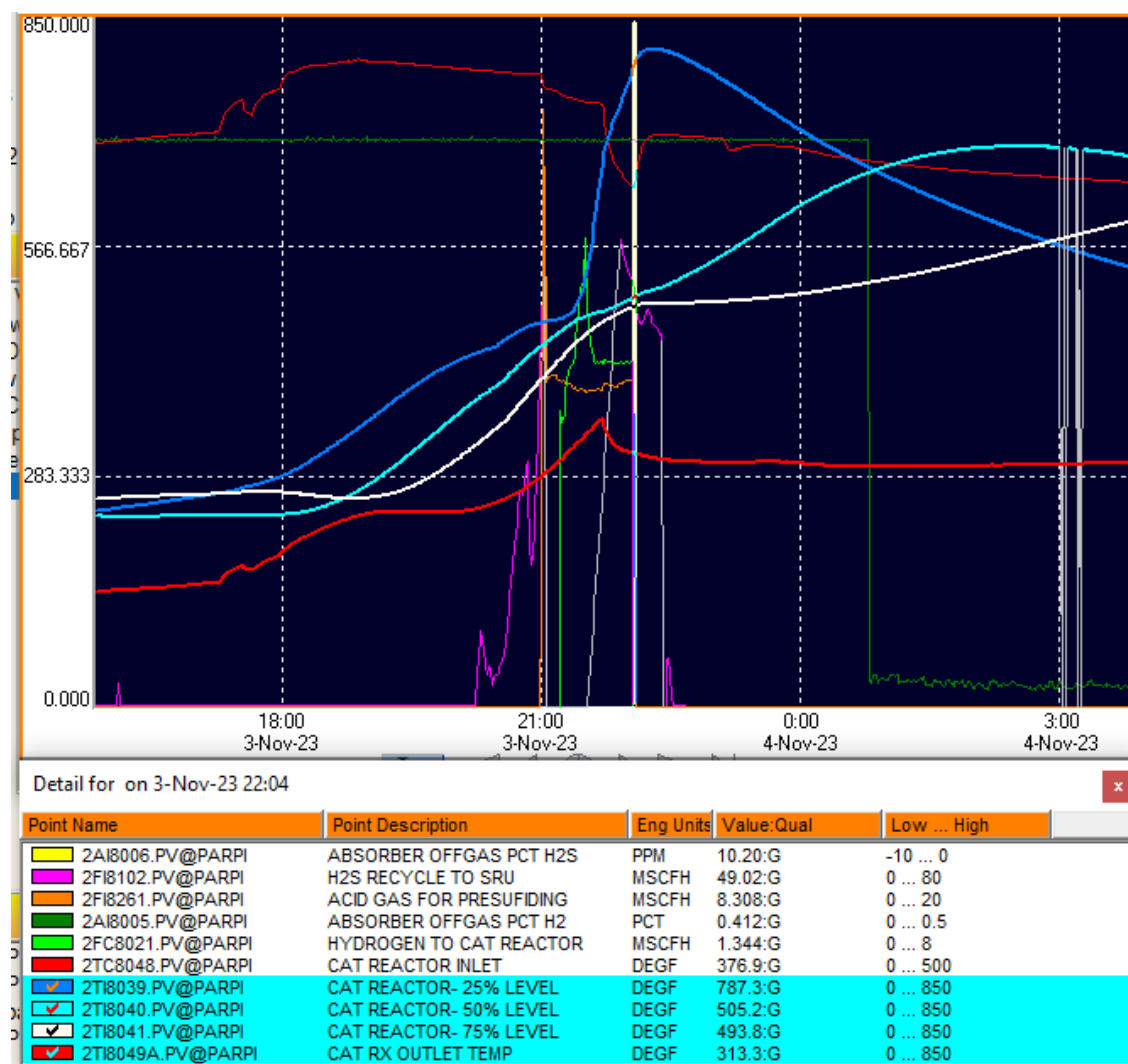
Sulfiding AG stopped

H2 stopped

Reactor cooldown initiated

Exotherm immediately peaked and turned.

Cooldown continued and regrouped until following day



Sulfiding Low Temperature TGTU Catalyst - Summary

- Sulfiding Low Temperature TGTU Catalyst with this approach accomplished the two objectives.
 - Maintained H₂S throughout the Reactor while sulfiding thus preventing H₂S starvation.
 - Reached desired Reactor Bed Temperatures >600°F with Reactor Inlet Temperature <315°F.
- Special thank you to ASRL, Rob Marriott, Chris Lavery, and Michael Huffmaster.

References

- 1) **UNDERSTANDING THE FORMATION OF AND HANDLING OF H₂S AND SO₂ EMISSIONS FROM LIQUID SULPHUR DURING STORAGE AND TRANSPORTATION** – Sulphur Seminar 1999 –Jan A. Lagas, Stork Engineers & Contractors B.V.; P.D. Clark, G.D. Butlin and E. Fitzpatrick, Alberta Sulphur Research Ltd.; M.L.J.A. Wetzels and W.S. Kijlstra, Shell Global Solutions