EXPERIENCES WITH NORCO'S SRU+SCOT TRAINS

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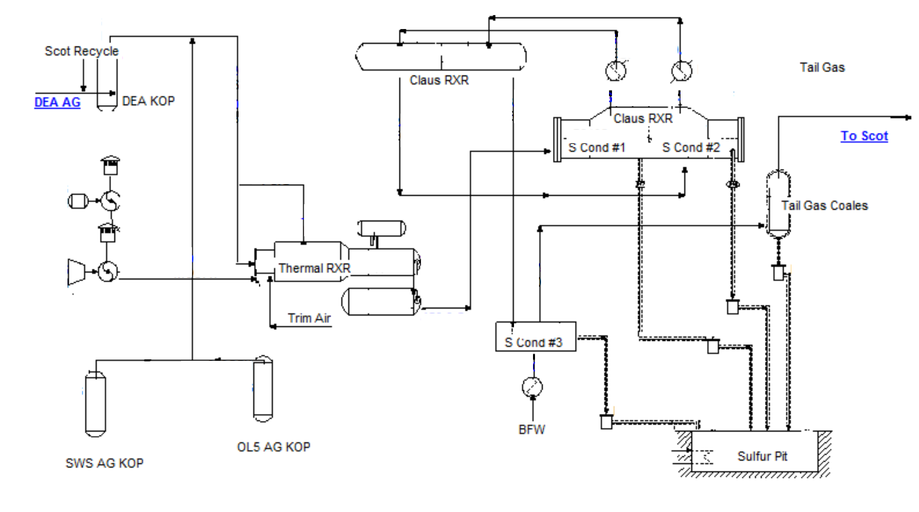
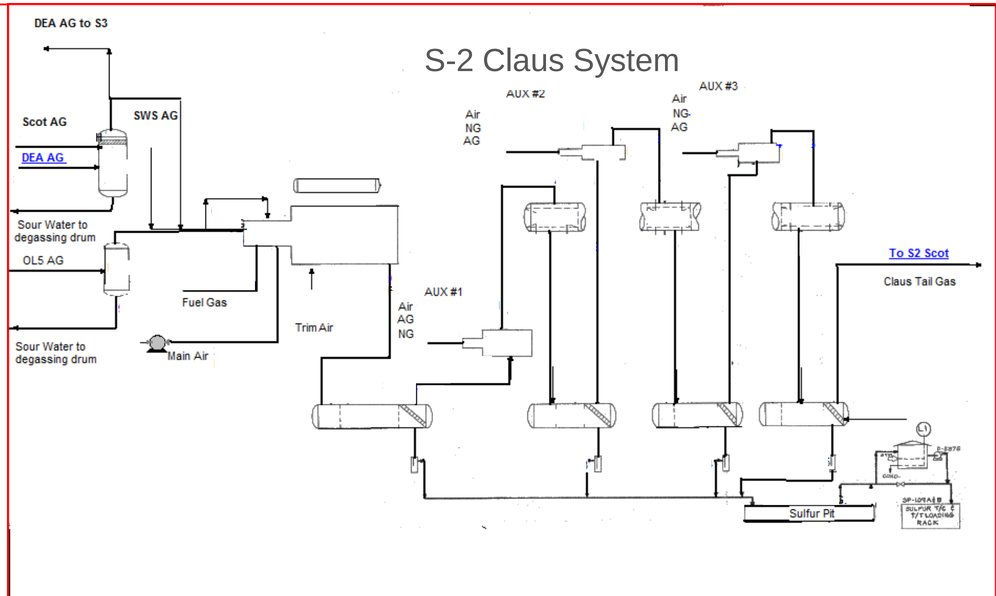
PRESENTATION OVERVIEW

- Description of Norco’s SRU+SCOT lineups
- Utility Buffer system → dedicated systems at each SCOT
  - Switch from anhydrous to aqueous buffer
- Norco’s SRU header system
- Upsides and Downsides of feed-linked SRUs
  - 2011 Quench Plugging event
  - 2012 S-3 SCOT Foaming Event

OVERVIEW OF NORCO'S SRU'S
2 SRU+SCOT Trains



S-3 Claus System



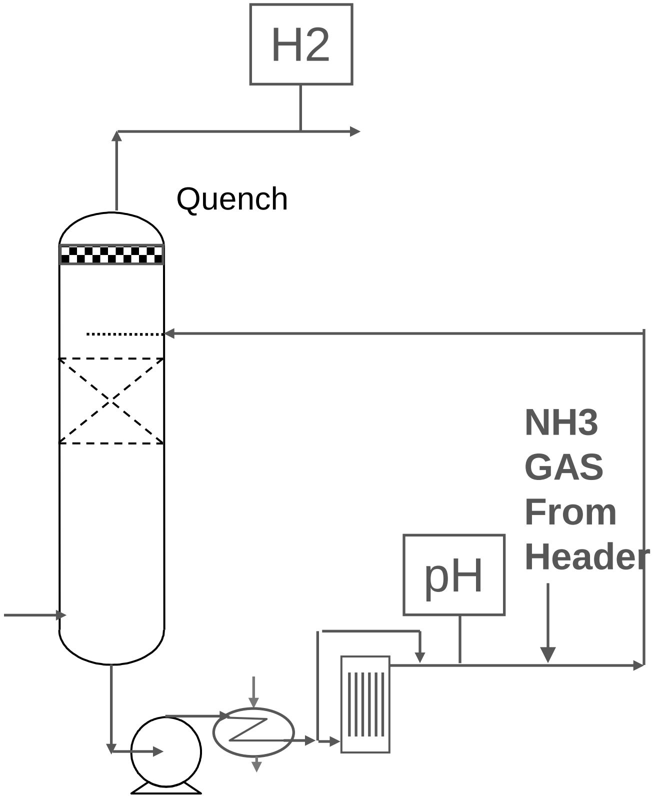
- S-3 is newer train (ca early 1990's)
  - 2-zone, ammonia-destroying T.R.
  - 2 stages, steam reheat, upsized WHB (hi P steam)
  - Pancake SCOT reactor, quench + MDEA system
- S-2 is older train
  - 2-zone, ammonia-destroying T.R.
  - 3 stages, AG or NG fired reheat, small WHB (med P steam)
  - Radial SCOT reactor, quench + MDEA system

SCOT QUENCH PH BUFFER SYSTEM

- Original system was
  - Single source (storage)
  - Anhydrous ammonia vapor
  - Feeding multiple uses inside the refinery (not just SCOT)
  - Comprised 6500 ft of pipe
  - Header managed by the Utilities group
  - Ammonia delivered in truck quantities

OLD SCOT BUFFER SYSTEM

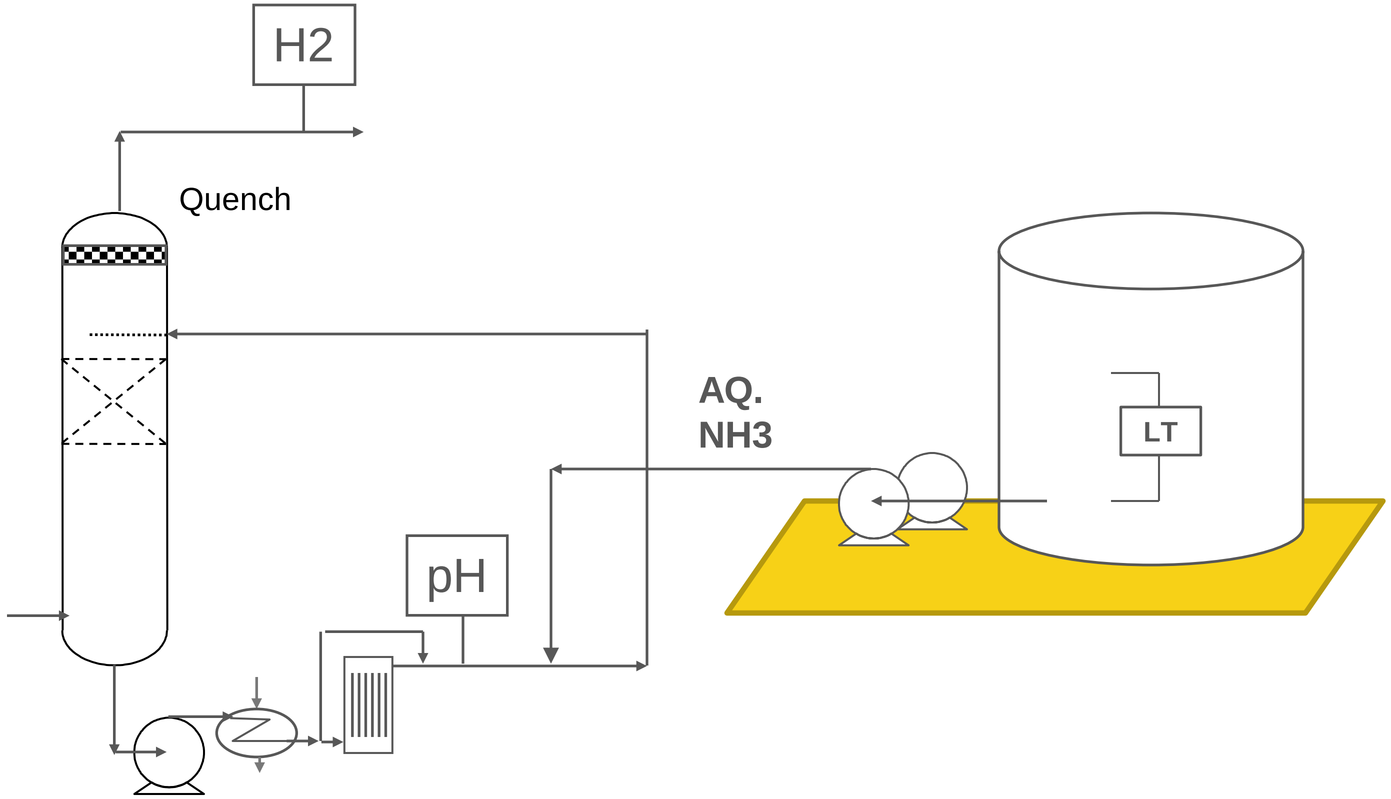
- Over the years
  - Other refinery users went away
  - Keeping the NH3 pressurized and ready at need, for the rare demand in the SCOT units
    - Meant dead legs throughout the refinery
    - Created an inspection headache
    - Came with risk of a leak, in locations where operator awareness was low (where NH3 was not consumed)
  - Simply – the system was overkill and was no longer the best way of meeting the needs at the SCOT plants



NEW SCOT BUFFER SYSTEM

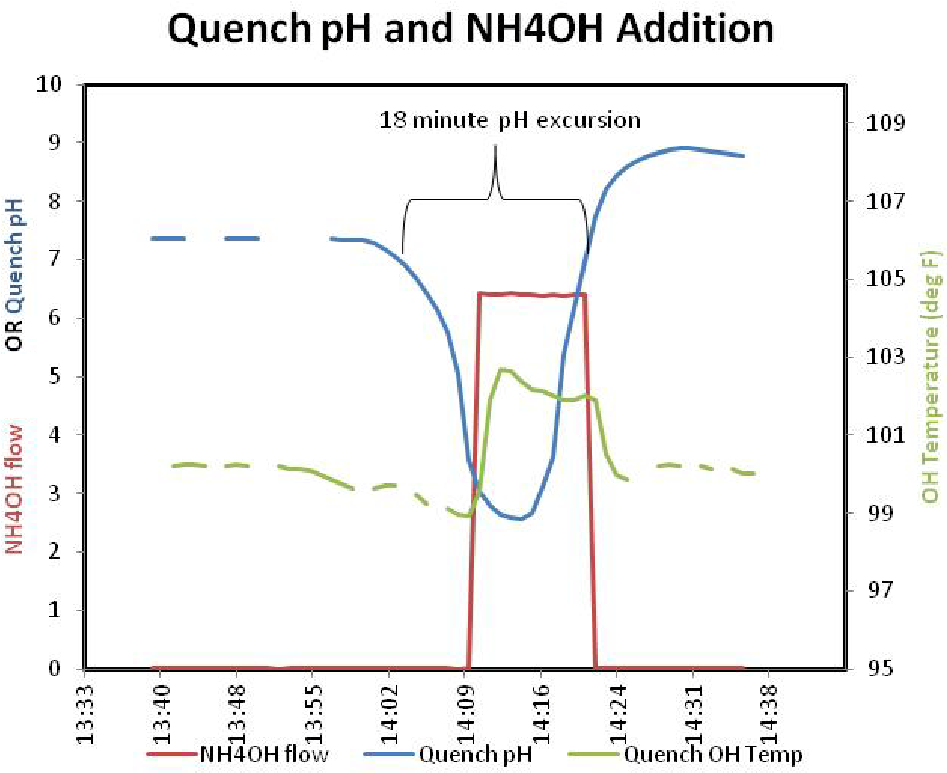
- Project to replace the old system with a fit-for-purpose system
- Aqueous Ammonia chosen
  - Ease of delivering buffer into the plant
    - pumping a liquid vs. relying on flow from a low vapor pressure gas
  - SRU/SCOT operator control of system
    - Two identical systems, one at each SCOT
- Old injection points re-used – into circulation loop

NEW SCOT BUFFER SYSTEM



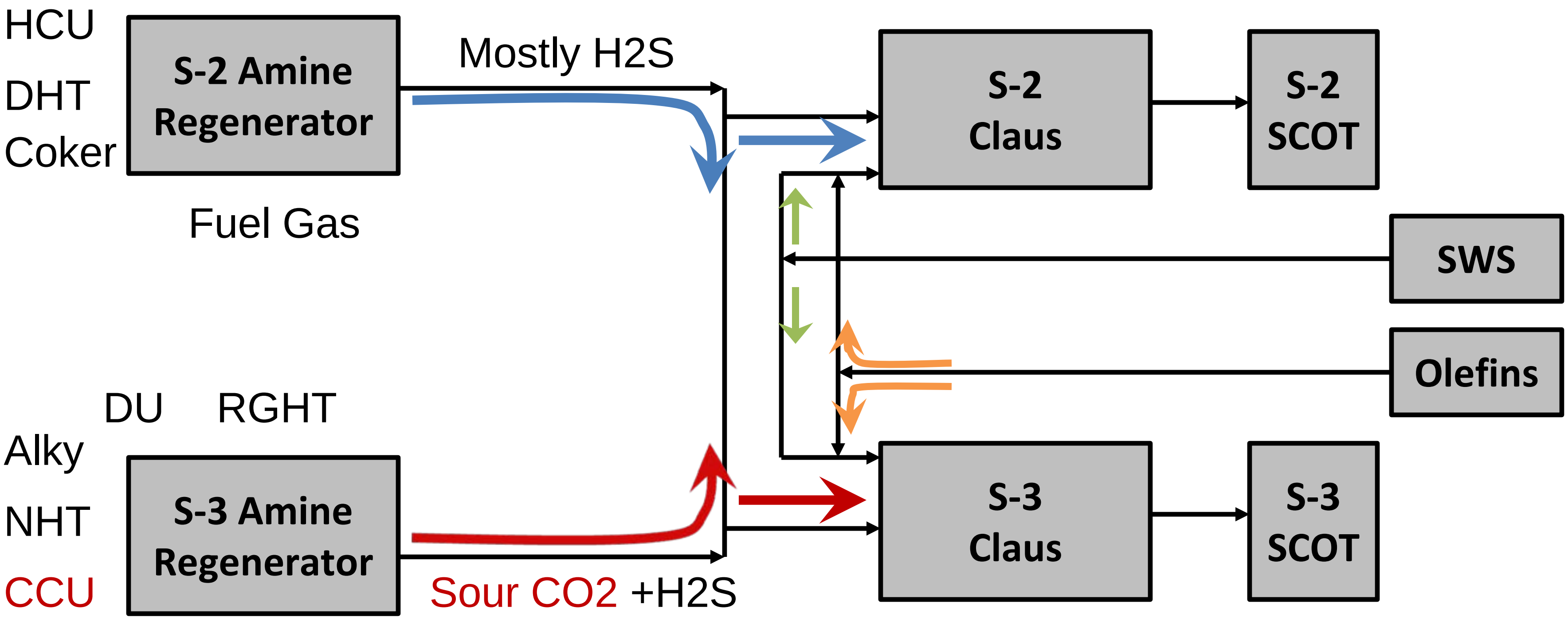
NEW SCOT BUFFER SYSTEM

- Lookback
  - Advantages
    - Easily monitored injection rate
    - Localized footprint
  - Areas for Improvement
    - Manual pump start



HEADER SYSTEM

NORCO'S SRU-SCOT / ACID GAS HEADER



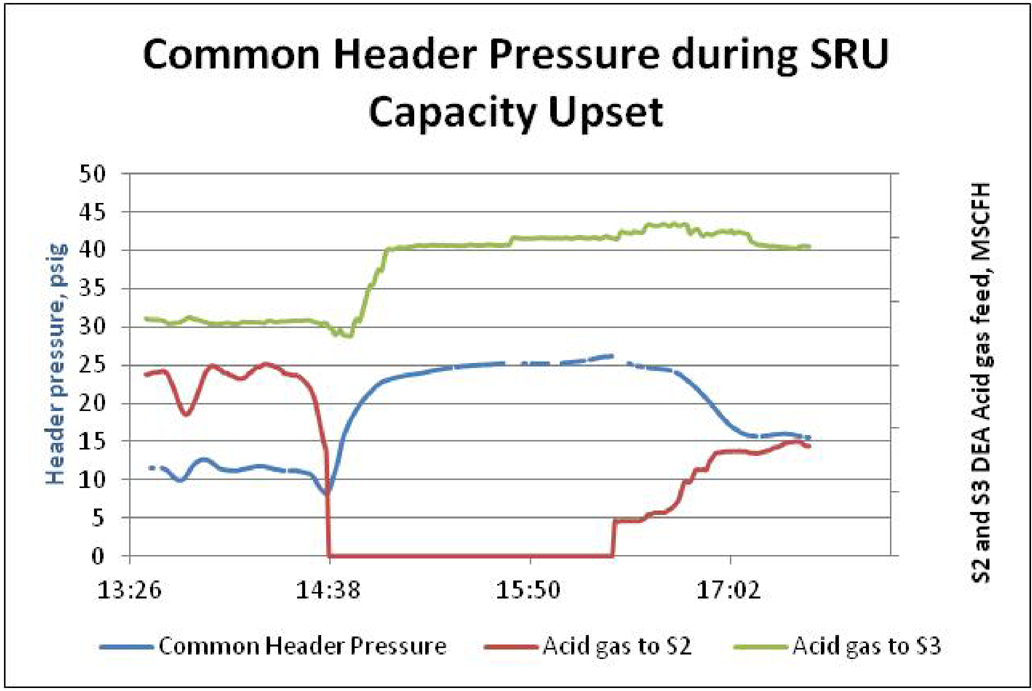
Ideally:
Both SRU's are operating, and each SRU consumes its own acid gas source
SWS gas can feed either, or both, SRU's at need
Olefins acid gas can feed either SRU at need, but preferentially goes to S-3 SRU

ACID GAS HEADER

- Both a blessing and a curse
- Upsides are widely recognized: Flexibility & Reliability
  - SRU's readily spare each other
  - Load shift between SRU's is rapid
  - Shifting load is easier than by shifting rich amine → less chance of a product impact due to regenerator upset
  - One SRU can run on flow control (easy); the other on pressure control (noisier)
  - 'Packing' of acid gas header gives operators a bit of time to react before triggering sulfur shedding

EXAMPLE OF COMMON HEADER PACKING

- S-2 SRU stops taking acid gas
- Both ARU's still producing normal load
- Header pressure rises to store acid gas without flaring
- S-3 SRU begins to take more acid gas feed to stabilize header



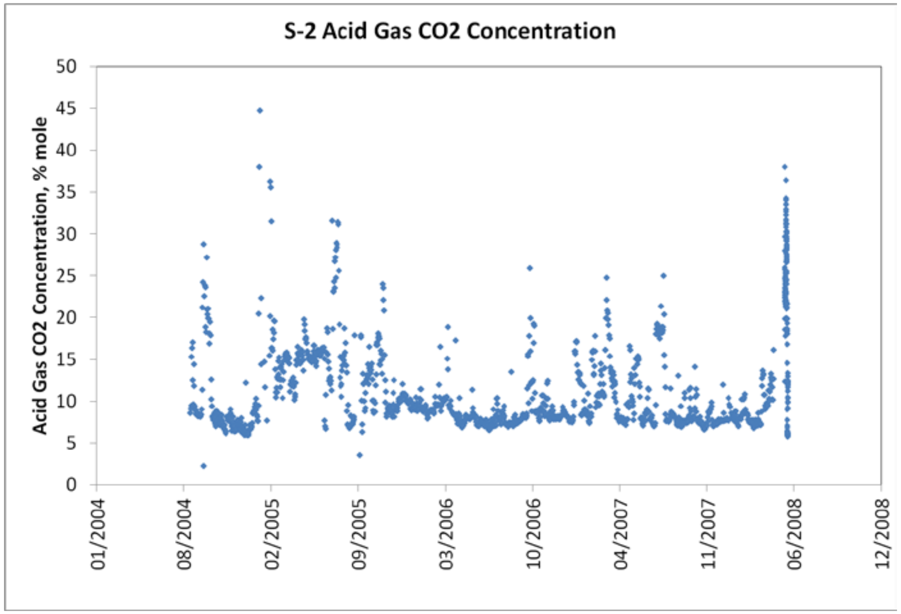
ACID GAS HEADER

- Downsides
  - Events Propagate (at least, in our system)
    - Upsets in one ARU can hit BOTH SRU’s
  - Load shifting comes with variation in conditions in the SRU’s
    - SRU’s don’t like variable feeds
    - If load shifts quickly, it can trigger upsets
  - Complexity – too many flow meters that don’t agree
    - It can be a struggle to close material balances, e.g. reconcile AG rates versus Sulfur Production

ACID GAS HEADER – FEED COMPOSITION

Acid Gas concentration varies when load shifts between SRU's

- Effect on Thermal Reactor temperature for NH3 destruction
- Effect of load on SCOT (CO2 in tail gas)
- Rapid changes challenge Air Demand control
  - Feed forward based on flow
  - Feedback responds to composition changes
  - Rapid composition change can put air demand out of balance



→ 2004 – 2008 reconciliation of Pit sulfur production and acid gas

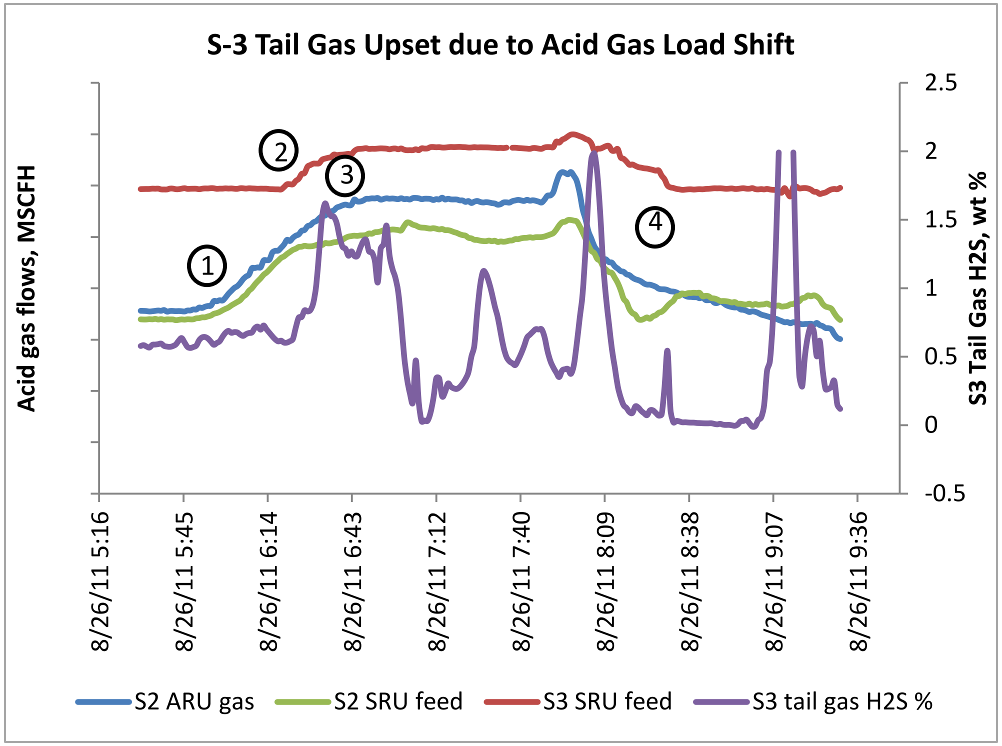
→ Can be very large variation in Acid Gas concentration when load shifts

ACID GAS HEADER – TROUBLE PROPAGATES THROUGH THE HEADER

- DHT event; stratified tank, huge increase in sulfur load
  - Acid gas from S2 to S3 dramatically increases
  - Air demand challenges
  - Loss of S3 tail gas ratio control
  - Quench pH impact
  - Quench loop plugging
  - pH Buffer system saves the day

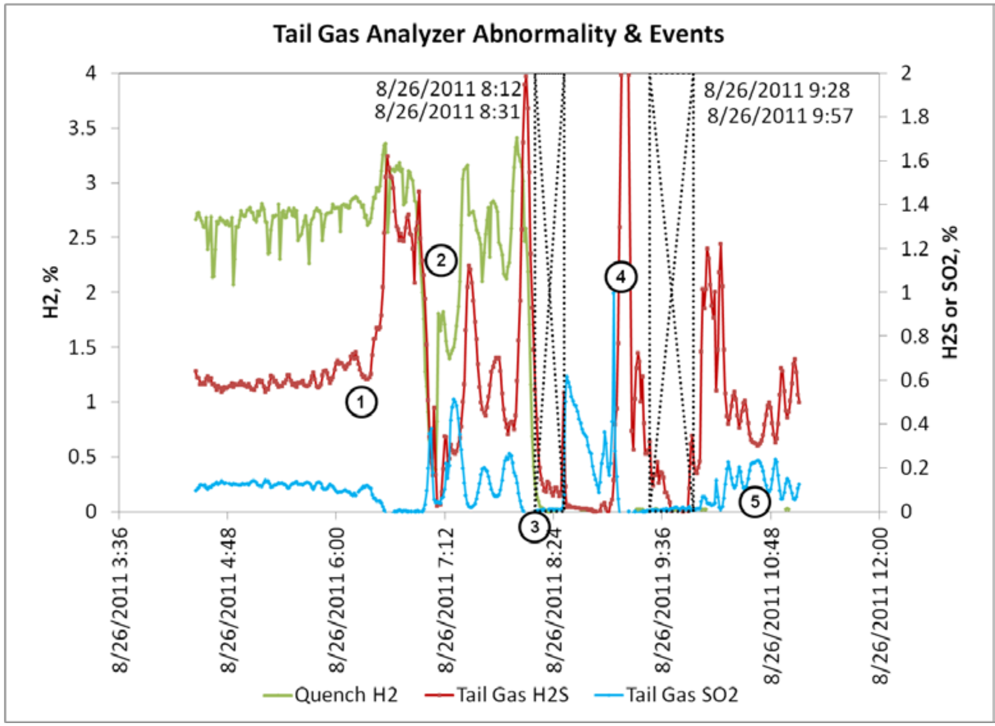
ACID GAS CHANGE FORCES SRU RE-BALANCING

1. S-2 ARU Acid gas increases, sends gas to pressure controlled S-2 SRU
2. S-3 SRU manually accepts more acid gas through header
3. High H2S in S-3 SRU tail gas is beginning of air demand swings
4. Several hours of upset through S-3 SRU train even with decreased acid gas load on unit



ACID GAS RATE INCREASES, AIR DEMAND CHALLENGED

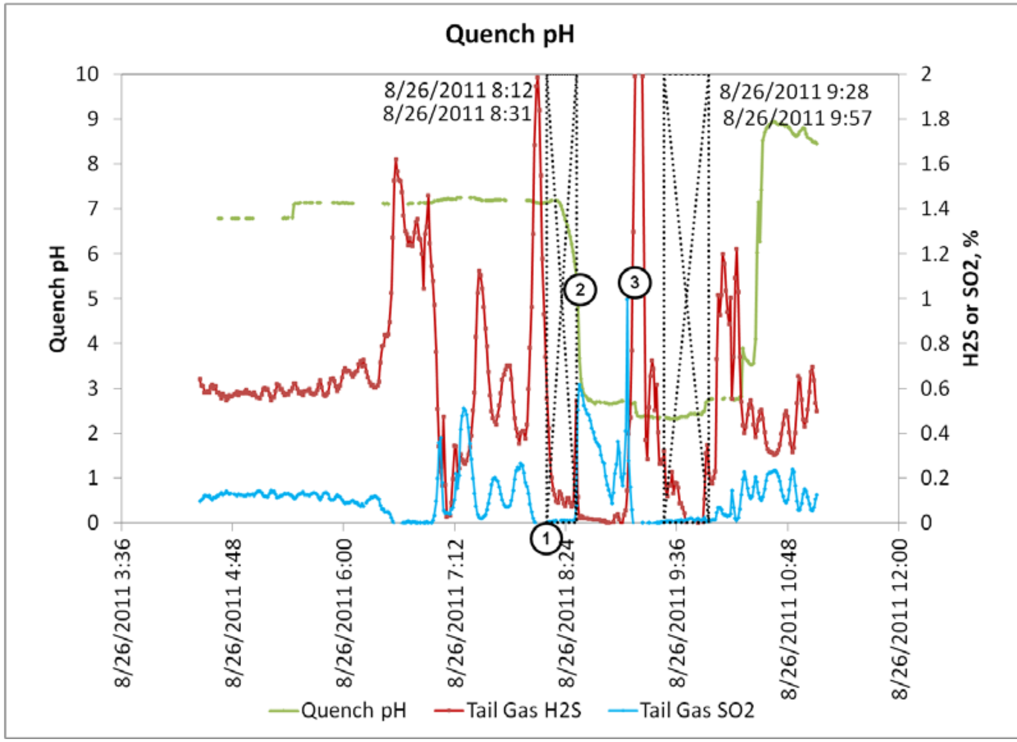
1. Acid Gas Rate to S3 jumps 15%
2. Air-long: H2 in quench ovhd drops (make less, consume more)
3. Tail gas analyzer fails – VERY air long
   - Lots of SO2
   - No H2 leaving quench
4. Air demand in Manual
   - Lots of H2S
5. H2 analyzer not working
   - Making H2, not consuming it but don't see it



AIR DEMAND CHALLENGE → QUENCH PH DROPS

1. Air-long
   - LOTS of SO_2
   - Not making much (any?) H_2
   - SO_2 slips into quench
2. Quench pH falls
3. Air put in Manual – Air Short
   - Excess SO_2 eliminated
   - H_2 restored (analyzer offline)
   - Quench pH does not recover

SO2 saturates Quench water, drops pH



QUENCH DP

1. Low pH quench (saturated with SO2)
   - Not much H2 make
   - Very little H2S
   - A little bit of DP build in Quench

2. Air in Manual – Huge amount of H2S into the quench

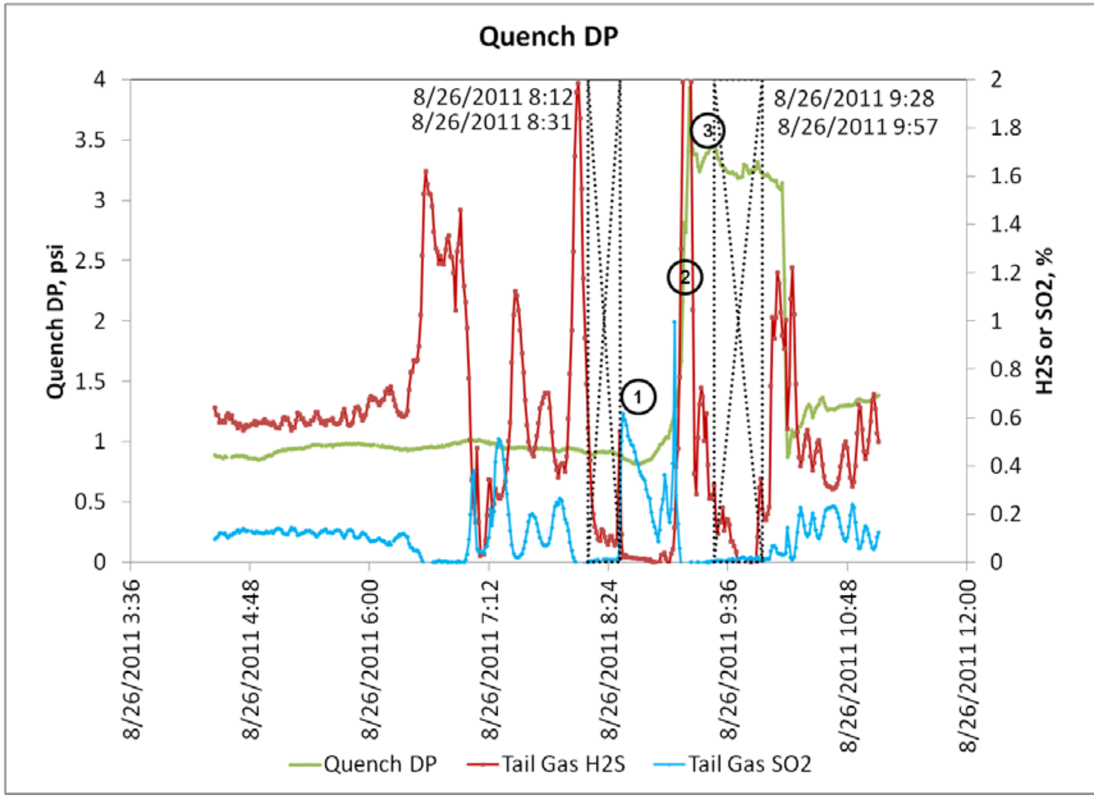
3. <u>Quench plugs rapidly </u>after

SO2 w/o H2 → no reaction

SO2 w/o H2S → no reaction

H2S + SO2 → Sulfur

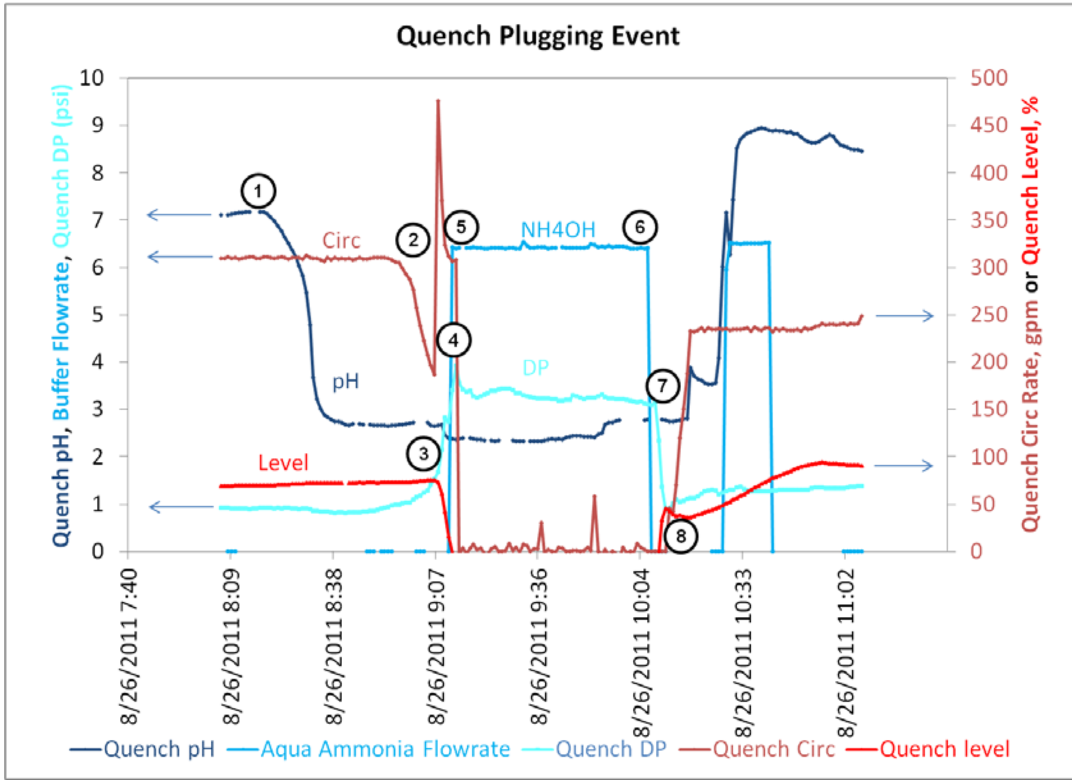
Quench DP rises when sulfur fouls



DURING THE PLUG EVENT

1. pH begins to drop
2. Filters plug, bypassed
3. Slow increase in DP, accelerates as filters bypassed
4. Sudden jump in DP
   - Quench level lost
   - Quench circ stops
   - pH & buffer inject – circ loop
5. Aqueous Ammonia flow on
6. Aqueous Ammonia flow off
7. Quench DP recovers
8. Quench Level and Circ recover
   - pH meter gets feed again

High pH reverses Quench DP; restores flow



LEARNING FROM THE EVENT, #1

- SRU's don't respond well to rapid changes in feed rate or composition (as is well recognized)
- With the header in place, both SRU's are subject to common modes of upset
- H_2 is needed to convert SO_2 over the tail gas catalyst; in this upset event, the native level of H_2 wasn't enough to react away all the SO_2
- Plugging of the quench was in progress, before the H_2S spike in the tail gas occurred.   The spike in tail gas H_2S meant a lot of SO_2 in the quench together with a lot of H_2S = a lot of potential to make sulfur

LEARNING FROM THE EVENT, #2

- Buffer injection into the quench circulation loop doesn't help if the quench is plugged (can't circulate NH_3)
- pH measurement in the quench circulation loop doesn't help if the quench is plugged (can't circulate sample loop)
- Buffer can minimize (partially reverse) sulfur plugging in the quench
- Aqueous ammonia vs. anhydrous
  - can get Aqueous ammonia to flow into column (via its own pump) even when quench circulation stops
  - Anhydrous needs help --- dissolves at point of injection, needs a carrier

S-3 SCOT FOAMING EVENT

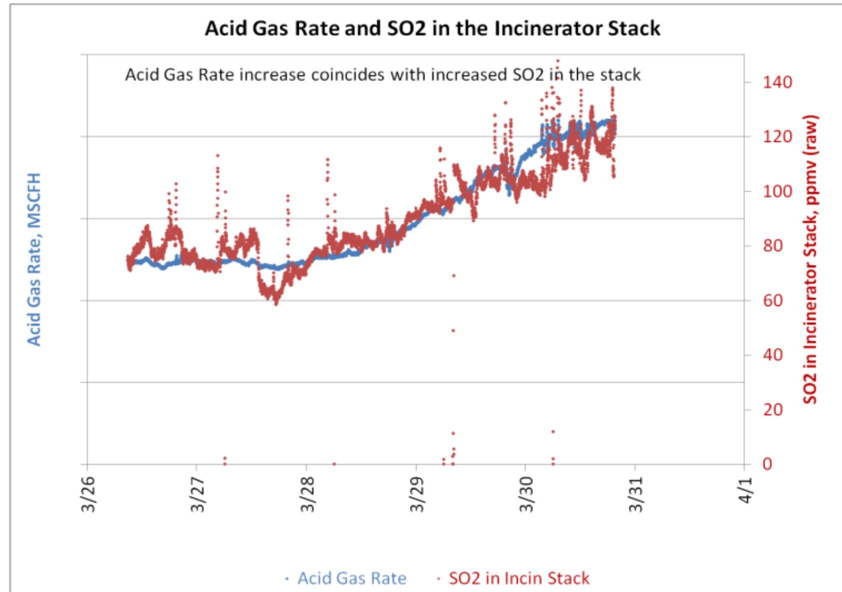
LEADING UP TO THE EVENT

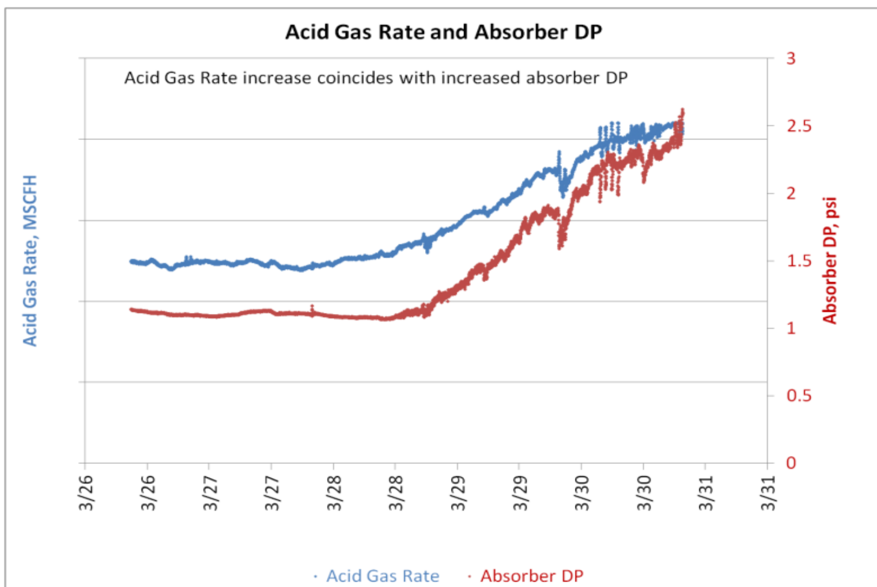
- S-3 SRU+SCOT processes sour CO_2 and a poor quality Olefins acid gas
- S-3 SCOT has a history of foaminess, compared to S-2 SCOT
- Operators have learned that amine strength >50%wt calms the system down
- Immediately before event, operators begin removing solvent to send batch to offsite reclaiming because of heat stable salts

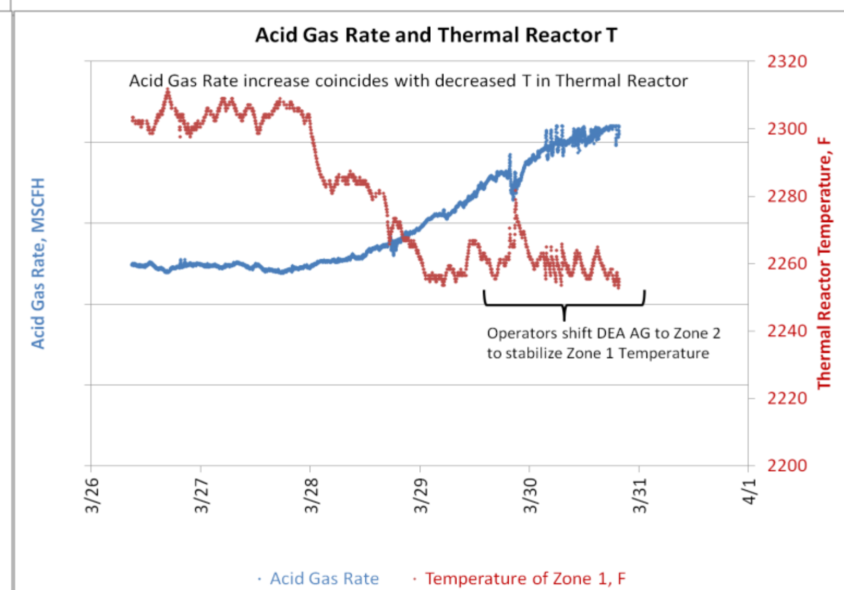
THE EVENT

- Absorber DP began increasing – but not very erratic
- Acid Gas Rate began increasing
- SO2 in Incinerator Stack increases
- Increased recycle lowers T.R. Temperature

→ unit increasingly vulnerable to upsets; less ‘surge’ capacity







INTERVENTION: NORCO’S FOAM FIGHTING TACTICS

Shock

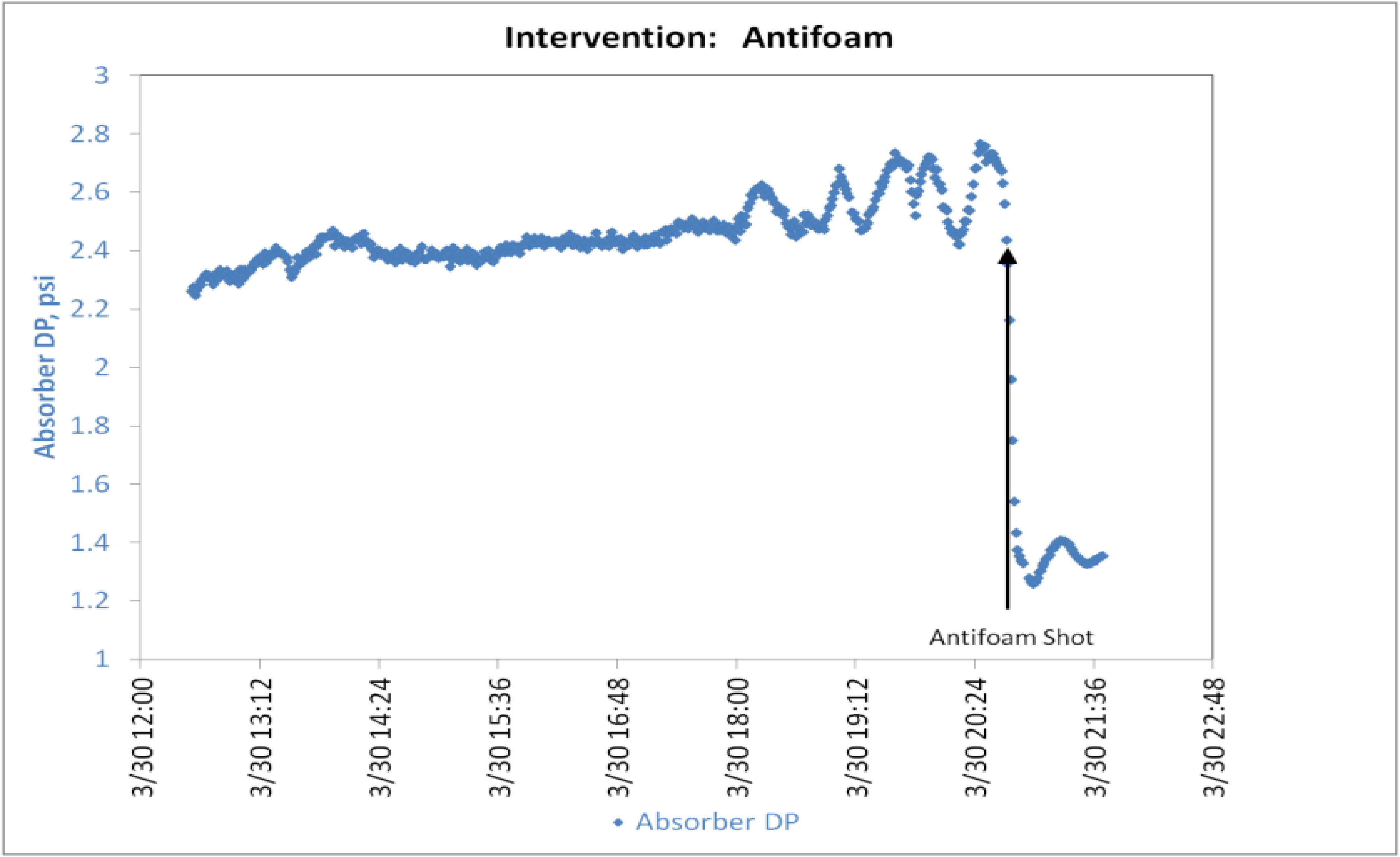
- Change Pressure
- Change Flow
- Change Temperature/water concentration

No Effect

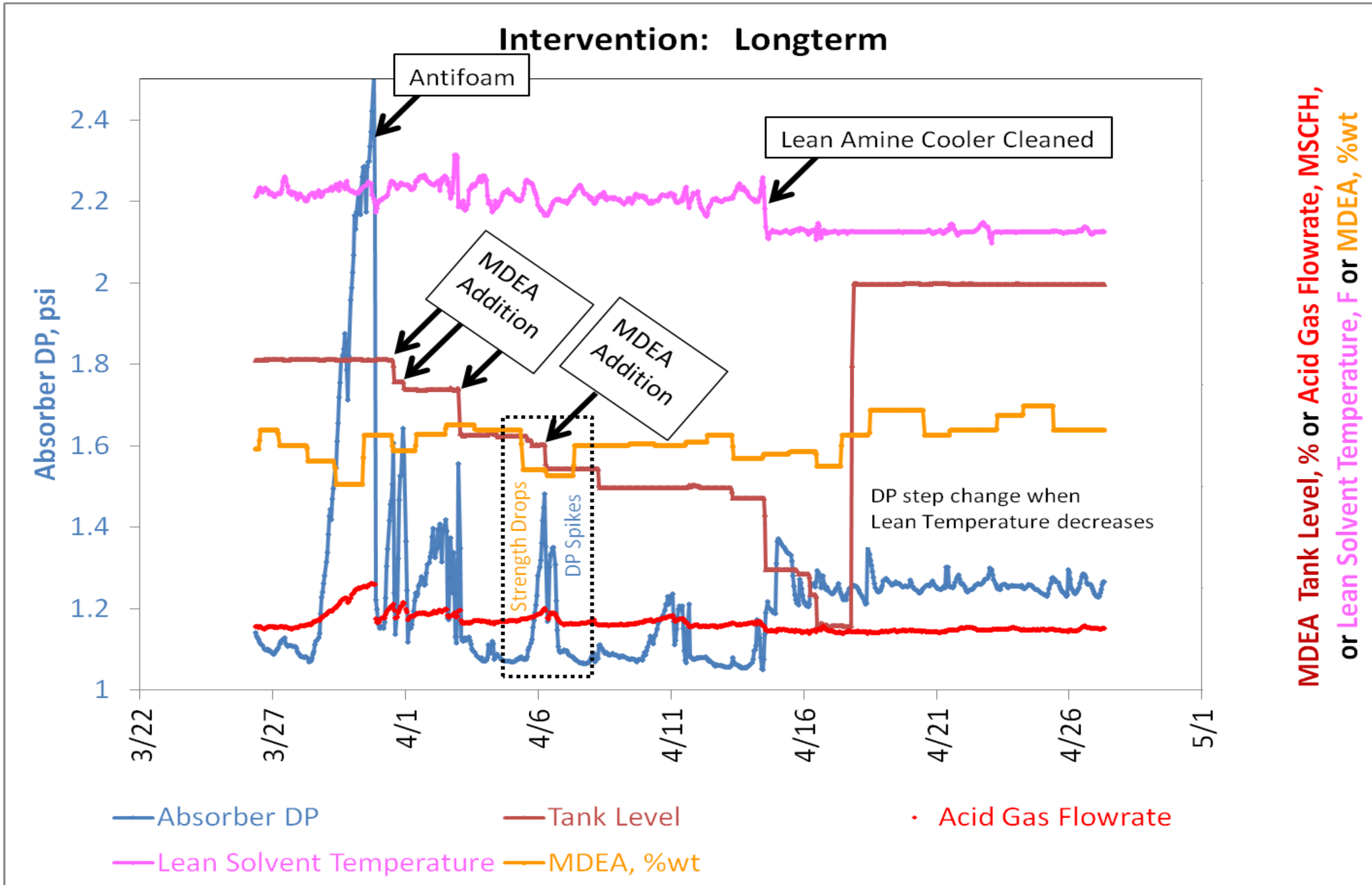
Add/Water/Escalate

- Add: Amine, or Antifoam, or Activated Carbon
- Water reject (heavy purge of reflux)
- Escalate (troubleshooting assist; aggressive reclaim or solvent replacement; evaluate plant features, etc)

ANTIFOAM DOSE



LONGER-TERM ACTIONS



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WHY DID THE ACID GAS RATE INCREASE?

- Is it real? (Yes – many points of evidence)
- A number of theories proposed:

1. The SCOT unit experience~~d increasing acid gas in the f~~eed to the absorber, possibly due to changes in feed gas to the SRU or due to decreased sulfur recovery in the SRU
2. The acid gas content of the absorber inlet was normal, but the SCOT absorber lost selectivity – and started acting as a CO2-pickup device. An especially-concerning subtheory during the event was that the SCOT absorber dP increase might be due to tray fouling, which might require a shutdown to remedy
3. The SCOT absorber was entraining feed gas with the rich amine

WHY DID IT FOAM?

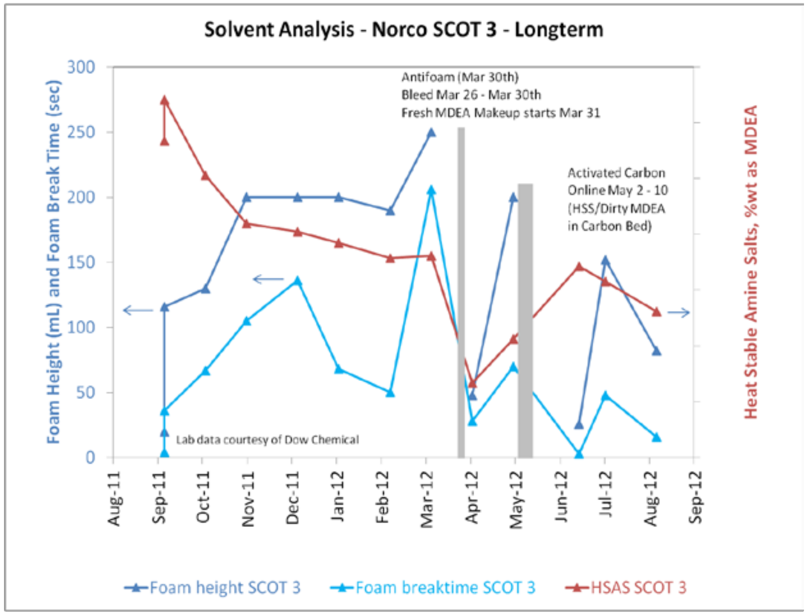
- Clues from laboratory foam tests

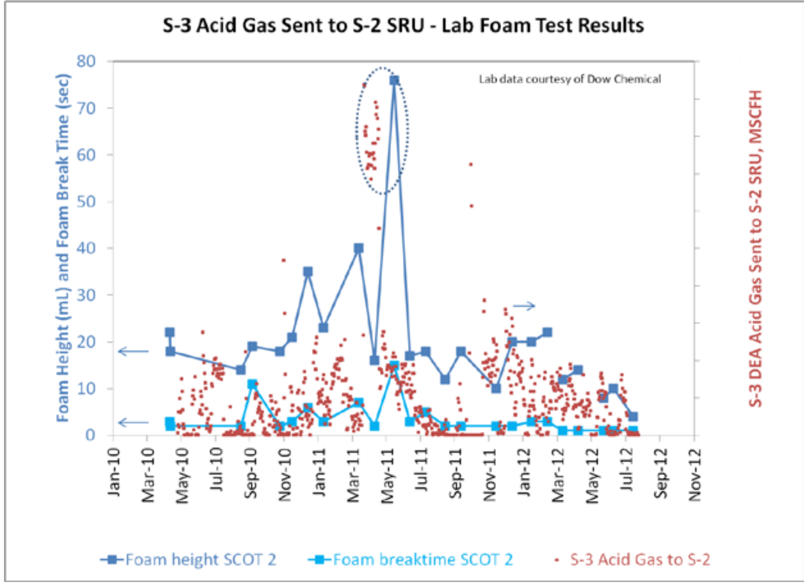
  → something builds up

  in the solvent

- Clue from swapping load in the header + laboratory foam tests

  → S-2 started to show foaming when processing S-3's feeds





BELIEFS AND BARRIERS VERSUS OBSERVATION

- Beliefs
  - Tail Gas Treaters are CLEANEST amine service. Some believe: because the process doesn't see liquid hydrocarbons, foaming is not a serious concern
- Barriers: Acid Gas through to the SCOT Absorber
  - Generously knocked out
  - Combusted at high temperature
  - Flow through more than one bed of high-surface area material (alumina catalyst)
  - Repeatedly sulfur washed (ie, in sulfur condensers)
  - Hydrotreated
  - Water washed (in the quench)
- Yet foaming happens in S-3 SCOT

LEARNING FROM THIS EVENT

Specific to this unit

- Low amine strength in this SCOT unit increases its tendency to foam.
- When doing an online solvent replacement in this unit, do it in smaller steps – in order to keep the amine strength up. Doing so will ‘throw some baby out with the bathwater’ but it will minimize the risk of increased foaming.
- Norco’s foam-fighting tactics worked. In this case, antifoam, addition of amine.
- Longer term, Norco can use the carbon bed when the supplier foam test starts to show increased foaming tendency.

LEARNING FROM THIS EVENT

General Observations

- This experience shows that tail gas treating units can be susceptible to foaming
- When DP builds in tail gas treating absorber, loss of selectivity can occur
- A clue exists at Norco: the quality of the feed to the SRU may be a factor in SCOT foaming despite the ‘barriers’ to pollution of the amine unit

CONCLUSIONS

- Experiences with Norco's SRU+SCOT were shared that showed
  - How header-linked SRU's can react to flow/composition changes
  - Having SRU's so linked means that upsets can move through the header
  - How Norco's SCOT unit responded during a header-triggered process upset
  - How Norco's new aqueous ammonia buffer system allowed the operators to reverse plugging of the quench during an upset
  - How foaming in Norco's SCOT unit decreased selectivity and increase recycle rate

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Q & A