Sulphur Plant Startup and Shutdown

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Introduction

- SRU startup and shutdown methods vary from company to company & facility to facility
- General guidelines and considerations used as the basis for the various procedures are common, for the most part
- Some procedures used entail more risk than others. DO NOT RUSH is the best rule ----> avoid the “Hurry Up and Wait Syndrome”

Introduction

- Best to address considerations, point out the risks involved and let the operator make his own decisions regarding acceptable risks with his “eyes open” for his particular circumstances
- In general, following proven methodology for startup and shutdown (mostly learned at the “School of Hard Knocks” by our predecessors) makes life easy. SRUs are very tame when the basic rules are followed, but unforgivingly harsh if shortcuts are taken.

Startup Considerations

- Two classifications : cold and hot
  - Cold: > first time SRU startup

    > previously run/ conditioned SRU (i.e. prepared for opening to atmosphere)
  - Hot > shut down for a number of days (no conditioning of catalyst/removal of sulphur gases

    > “hot standby” if recycle available (Recycle Selectox or COPE), or SRUs with high turndown burners and fully automated controls

Cold Startup: verify equipment first

- Air blowers - surge control operable?
- Mainburner - natural gas controls operable?
  - air purges operable?
  - ignitor operable?
- RF/ WHB - refractory/ checker wall inspected?
  - WHB tubes leak checked?
  - tubesheet ferrules - condition?
  - debris removed?
- Catalyst Beds - catalyst depth uniform?
  - ceramic ball support layer in?
  - fresh or used catalyst?
  - grating support in good condition?
  - debris removed?

Cold Startup: verify equipment first

- Condensers - tubes leak checked?
  - demister pads in? multi-density?
- Inline Burners - gas control system operable?
  - ignitor operable?
- Indirect RH - tubes leak checked?
  - if gas fired, controls operable?
- Seal pots/ sulphur storage pit
  - debris removed?
  - steam coils in? steam jackets on?
  - melt sulphur on the outside?
  - sulphur pumps operable?
  - seals pre-loaded or loaded after startup?

Cold Startup: verify equipment first

- Steam Jackets
  - are they all on?
  - do they melt sulphur on outside?
  - traps on new systems blown for 24 hours?
- Incinerator - refractory checked?
  - burner checked?
- ESD System - checked and tested?

Cold Startup: air blows

- If fresh catalyst has been installed, then blow the reactors in sequence:
  - block reactor outlet pipe --- temporary wooden cover
  - open manway on reactor outlet side
  - using air blower, blow out dust to atmosphere
  - sweep clean or vacuum bottom of converter and close --- don’t forget to remove temporary wooden cover
  - some have used pressure / de-pressure cycles as well

Cold Startup: air blows

- For a new plant or for any new sulphur seals, I also recommend air blowing them:
  - block sulphur pipe leaving the “look box” with a rag
  - open and close the condenser rundown valve (with blower on) a number of times to vent dust to atmosphere through the open look box

    --- don’t forget to remove the rag when done

Air blows minimize the risk of forming “sulphur concrete (sulcrete)” in the rundown systems --- restricts and/or blocks sulphur flow

Cold Startup

- Heat up (preliminary) the SRU using the air blower:
  - air is at 160 to 250ºF [70 to 120ºC], depending on ambient and whether or not SRU has an air preheater
  - desireable to have catalyst beds at > 160ºF [70ºC] prior to firing any of the burners (water dewpoint at 120 to 140ºF [49 to 60ºC] for flue gases from a stoichiometric natural gas flame)

Cold Startup

If the SRU has new refractory or has had major repairs done to the mainburner/ reaction furnace refractory, then a dryout must be done. Procedures vary -- check w/ refractory manufacturer. Typical procedure:

- heat up to 250ºF [120ºC] at 50ºF [30ºC]/hr and hold for 2-4 hours
- heat to 350ºF [175ºC]- same rate - hold for ~20 hours
- heat to 600ºF [315ºC]- same rate -hold for 5-10 hours
- heat to 1000ºF [538ºC] - same rate -hold for 5-10 hrs
- control any cooldowns at 100ºF [55ºC]/hr

Note: best to heat up all the way to normal operating temperature during dryout to ensure a proper cure

Cold Startup

For new converter (reactors) and incinerators (or thermal oxidizers), a typical dryout procedure is:

- heat up to 250ºF [120ºC] at 50ºF [30ºC]/hr and hold for 2-4 hours
- heat to 400ºF [204ºC]- same rate - hold for ~5 hours
- heat to 600ºF [315ºC]- same rate -hold for ~5 hours for converters; heat to 1000ºF [538ºC] at same rate and hold for ~5 hours for incinerators

I consider the above methods safe (i.e. to prevent refractory damage/ lift-off by slowly removing water)

Use of a temporary dryout heater system is best (e.g. Cooperheat). Otherwise use available burners.

Cold Startup

Speeding up dryouts can/ has resulted in refractory failures:

- hot spots after firing the mainburner
- SRU outage for repairs
- can cost another 4 to 6+ days of downtime

Cold Startup

Remember to keep the catalyst beds at > 160ºF [70ºC] when firing any burners upstream to eliminate risk of water damage during heat up

- system heat up to normal operating temperatures should be carried out at 50 to 100ºF [30 to 55ºC] per hour (DO NOT RUSH)
- use mainburner and inline burners firing at excess air (30 to 100 air to gas ratios)
- heat up by decreasing the air to gas ratio (don’t go too slow)

Cold Startup

- Recommended safety items on burners:
  - double block & bleed (automated) on natural gas
  - equip with high energy spark ignitors
  - light-off sequence to include a purge cycle (preferably N_2) and a 5 to 10 second time window for light-off
- Recommend automated natural gas control systems for all burners c/w ESD stations
  - natural gas flow for the mainburner can be used in the air demand calculation, using a factor of 9.5 to 10, by adding it to the acid gas air demand for use in feedforward control
  - use P & T compensation on air, acid gas & natural gas

Cold Startup

- Suggested order of actions to begin processing acid gas is then fairly straight forward:

1. Inline burners on natural gas at 95% of stoich
2. Pull acid gas blind(s), using all safety precautions
3. Increase natural gas to mainburner & decrease air flow until at 95-100% of stoich, using steam addition to moderate the temperature to < 3000ºF [1650ºC] (at 4-10 lbs [kg] of steam per lb [kg] of gas). Stay within burner parameters to prevent backfiring.

Cold Startup

4. Make sure that system temperatures are all above 250ºF [120ºC] (with > 300ºF [150ºC] preferred) and then introduce acid gas (rate at > low flow shutdown). If the system is automated, the controller will handle the air flow adjustments using the designated air to acid gas and air to natural gas ratios. If done manually, set the air flow per the air flow calculations (a very TRICKY operation).
5. Slowly cut the natural gas flow to the mainburner to zero, and turn off the moderating steam. DB&B both.
6. Switch any acid gas burners to AG from natural gas
7. Introduce the ADA to the system controls
8. Introduce any SWS acid gas to the mainburner

Cold Startup

If the sulphur seals were not preloaded with solid or liquid sulphur before startup:

- Open and close the condenser outlet valves every 15 minutes until the seals are filled (more often is best for the first condenser)
- Take precautions (gases contain up to 10% H_2S)
- Best by far to preload seals ... a number of Shell and ExxonMobil refineries have installed a sulphur flush system for all the seal pots (to eliminate the need to open the look boxes) and this system also allows them to preload the seals with liquid sulphur

Cold Startup

- Final step is to adjust bed inlet temperatures to achieve the design (optimum) bed outlet temperatures
- Final condenser at 255 to 265^{o}F [124^{o} to 130^{o}C], to minimize sulphur vapour losses
- A coalescer at the back can increase recovery by 0.1 to 0.2% ... less liquid sulphur entrainment
- Minimize O_2 in incinerator flue gas, typically to 2% excess oxygen (10% excess air)

Hot Startup

- Light off the mainburner at 95% of stoichiometry and use moderating steam to maintain <3000°F [1650°C]
- Light off inline burners at 95% of stoich and ensure that the catalyst beds are > 300°F [150°C] (>400°F [200°C] preferred)
- Introduce acid gas and back out natural gas/ moderating steam to mainburner (DB&B both)
- Switch acid gas burners to AG from natural gas
- Check catalyst bed pressure drops and increase inlet temperatures if too high
- Return to optimum operating temperatures

Hot Startup

Note:

- Some operators light off on acid gas if the Reaction Furnace temperature is still > 1600ºF [870ºC]
- Some will also allow light off on refractory above these temperatures
  - not recommended since the safe approach (lighting from a spark ignitor or a pilot gun) is not difficult or time consuming, provided good equipment is supplied to the operator

Shutdown Considerations

- Short Term or “Hot Shutdown”:
  - Emergency type (minutes to a few days)
  - System slowly cools
  - Use small nitrogen purge to prevent backwards air ingress ----> fires can result
  - Keep at less than 3-5 days to prevent crusting of the beds

Shutdown Considerations

- Another method is called “hot standby”:
  - For units with recycle blowers (e.g. Recycle Selectox, COPE)
  - For units with very high turndown burners and totally automated control systems
  - Can be maintained on hot standby almost indefinitely

Shutdown Considerations

- Long Term Shutdowns:

  Preparation for entry (opening to atmosphere)

  Suggested order of action:

  1. Heat soak the catalyst beds (50 to 80ºF [30º-45ºC] above normal) for 48 hours. Can also rejuvenate the beds (using between 5 and 6 to 1 H_2S to SO_2 ratios) during this step.
  2. Switch from acid gas to natural gas burns at 95% of stoich, with moderating steam to the mainburner
  3. Continue the “natural gas sweep” until all the sulphur flow stops (typically one to two days). Rod all rundowns to ensure no flow (prevents fires later)

Shutdown Considerations

4. 12 hours after sulphur flow stops, shutdown the inline burners
5. Slowly start increasing air to the mainburner:
   - hold at 1% excess oxygen for at least 6 hours (12 preferred)
   - can use an oxygen analyzer (upstream of catalyst beds)
   - decrease air if reactors heat up
   - shut off moderating steam when RF temperatures drop below 2400ºF [1315ºC]
6. When bed temps are <400ºF [200ºC], shut down mainburner. Continue air cooling until temperatures are below 250ºF [120ºC] (and de-pressure WHB /CDs)
7. Shut down blower and open the SRU manways.

NOTE: Good control essential for steps 2 to 5, above

Shutdown Considerations

- Burn Out or Regeneration Method:
  - Used to attempt to remove carbon from catalyst in conjunction with a standard natural gas sweep (done first)
  - Used to remove sulphur from catalyst
  - Raising bed temperatures to > 600ºF [315ºC]
    - low success rate
    - high fire risk … runaway temperatures are the norm
    - damage to catalyst and equipment likely

This method is NOT recommended

Shutdown Considerations

- Inert Quench Method:
  - Nitrogen Quench
    - Introduction of N_2 at 100 to 195ºF [40º to 90ºC] via mainburner, after heat soaks ... risk of freezing/ bed pluggage (risk mitigated w/ N_2 at > 250ºF [120ºC])
    - Rate at about 20% of normal flow, for about one day
    - Sulphur on/ in catalyst when complete (changeout)
    - Entry under mask only

Some plants have used natural gas sweep (to remove sulphur) followed by nitrogen purge to cool to 120ºF [50ºC] -- to speed up the cooldown

Shutdown Considerations

- Steam Quench Method:
  - Has also been used for rapid shutdown
  - Catalyst must be changed out (mush)
  - Corrosion concerns
  - Water in sulphur rundowns
  - Entry under mask only

Shutdown Considerations

- Shutdown of Sulphur Storage Pit (Tank)
  - Worry of H_2S at >LEL (~3.5% at pit temp.)
  - Concern is fire or explosion
  - Pits with normal inert vapour space:
    - Get H_2S to < 1% by increasing purge flow
    - Introduce sweep air
    - Lower pit level (have snuffing steam ready ... fire caused by pyrophoric FeS, present on carbon steel components)

Shutdown Considerations

- Pits with normal air vapour space:
  - Increase sweep air flow, ensure H_2S is at <1%
  - Lower pit level (have snuffing steam ready ... fire caused by pyrophoric FeS, present on carbon steel components)

TGTU Startup Considerations

- As with the SRU, the success of the TGTU startup is dictated by the care taken during Precommissioning

TGTU Startup Considerations

- TGTU Startups following a brief trip (SRU or TGTU) are typically straightforward
  - Maintain Quench loop circulation
  - Maintain Amine circulation and temperatures
  - Monitor catalyst temperatures (may need to heat before restart)
- The remainder of this discussion will focus on new TGTU Startups and Startups after Turnarounds

TGTU Startup Considerations

- Typical Sequence:
  - Amine system isolated from Hydrogenation / Quench system
  - Quench loop flushing and hydrogenation catalyst presulfiding done in parallel with amine system cleaning
  - Two systems joined just prior to startup

TGTU Precommissioning

- All vessels clean and free of debris
- All trays/packing installed per vendor instructions
- All pump seals filled
- All pump strainers installed (use temporary if necessary)
- If using fired Preheater (RGG), BMS checked

TGTU Precommissioning

- Fired Preheater (RGG)
  - Follow refractory vendor’s dryout procedure
  - Typical procedure
    - Heat to 250 F (120 C) @ 50 F (30 C) / hour
    - Hold ~ 4 hours
    - Heat to 520 F (270 C) @ 50 F (30 C) / hour
    - Hold ~ 4 hours
    - Cooldown @ 100 F (50 C) maximum
  - Can be done in parallel with Waste Heat Boiler boilout and catalyst presulphiding

TGTU Precommissioning

- Hydrogenation Reactor Refractory Dryout
  - Follow refractory vendor’s procedure
  - Typically the same as Claus Converter procedure
  - Typically done in parallel with RGG dryout

TGTU Precommissioning

- Hydrogenation Catalyst Presulphiding
  - Follow catalyst vendor's procedure
  - Typical procedure (assuming recirculation with acid gas connection)
    - Establish Quench circulation
    - Establish nitrogen circulation, maintain ~5 psig at blower/eductor suction
    - Ensure Oxygen content < 0.5%
    - For RGG, 95% of stoich maximum

TGTU Precommissioning

- Heat catalyst to 390 F (200 C)
- Start Acid Gas flow, then Hydrogen flow (if using make-up Hydrogen, sequence is important)
- Want 3% to 5% Hydrogen
- Monitor catalyst temperature wave
- Adjust Acid Gas / Hydrogen flows to control temperature if necessary
- Monitor Quench pH, use ammonia / caustic injection as necessary

TGTU Precommissioning

- When temperature wave has moved through catalyst bed, increase inlet temperature to 600 F (315 C) at a rate of 50 F (30 C) / hour
- Hold for ~ 4 hours
- Use stain tubes to verify H_2S concentrations at outlet > 1%
- Reduce catalyst temperature to normal operating
- Maintain recirculation or nitrogen blanket

TGTU Precommissioning

- Quench Loop flushing
  - Condensate or demin water preferred
  - If system is dirty, can use filters of decreasing mesh size (100, 50, 25 micron)
  - Monitor pump suction pressure
  - Alternate pumps

TGTU Precommissioning

- Amine system flushing
  - Condensate or demin water preferred
  - If flush water is dirty, may need to fill and drain system several times while flushing
  - Heat water to 140 F (60 C) using reboiler
  - Add soda ash or potash (typ. 1%)
  - Circulate for ~ 12 hours
  - Alternate pumps

TGTU Precommissioning

- Dump caustic solution and fill with condensate or demin water
- May take several rinse cycles to remove carbonates
- “Belts & Braces”... flush with 3% amine solution
- Fill system with normal strength amine
- Nitrogen blanket

TGTU Startup

- The TGTU Startup can follow immediately after Presulphiding and Amine system flushing
  - Stable RGG operation
  - Catalyst is at normal operating temperature
  - Amine system is hot and ready
  - Anti-foam injection system ready
  - Filters all in-line

TGTU Startup

- Stop recirculation and line-up for normal operation
- Typically the RGG is shut down when recirculation stops, and restarted just prior to tail gas introduction
- Some plants have bypass downstream of Waste Heat Boiler to Incinerator
- When all is ready, divert tail gas from Incinerator to TGTU

TGTU Startup

- Parameters to watch during Initial Operations
  - Quench water pH and color
  - Catalyst temperatures
  - Quench overhead hydrogen (2% to 4%)
  - Lean / Rich Amine color
  - Absorber / Regenerator dP

TGTU Startup

- Iron sulphide layer is formed in amine system during commissioning, so filters may plug...make sure extra sets are available
- Iron sulphide can cause foaming
- Anti-foam rule of thumb:
  - 10 ppmw for Silicone based
  - 100 ppmw for Glycol based
- Amine testing

TGTU Shutdown Considerations

- Short shutdown (few hours)
  - Monitor catalyst temperatures
  - Recirculate nitrogen if necessary
  - Maintain Quench and Amine circulation

TGTU Shutdown Considerations

- Longer shutdown (no equipment to be opened)
  - Set up gas recirculation loop and recirculate nitrogen to keep catalyst hot
  - Maintain Quench and Amine circulation
  - Nitrogen blanket on amine
  - Circulation can be stopped and plant kept under nitrogen for longer periods

TGTU Shutdown Considerations

- Long shutdown (equipment to be opened)
  - Maintain amine circulation and regeneration until rich loading equals lean loading
  - Isolate Hydrogenation / Quench system from Amine system and establish nitrogen recirculation to cool catalyst
  - Maintain positive pressure (~5 psig) in recirculation loop

TGTU Shutdown Considerations

- Catalyst is in the reduced state and is pyrophoric so it must not come into contact with oxygen
  - Can be removed under nitrogen blanketing (typically by third party)
  - Can be oxidized in the reactor (refer to vendor procedures)
- Follow all site vessel entry procedures (steam-out, nitrogen purge, blinding, etc.)

Final Comments

We hope that this review has been informative and useful.

As with all opinions on matters of startup and shutdown, we are sure that some will differ with the opinions expressed ... but not with the substance.