TECHNICAL REVIEW:
ENAP ACONCAGUA REFINERY SULFUR BLOCK

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ABSTRACT

The ENAP Aconcagua refinery is located in Concón, on the Pacific coast of Chile, and over the years residential development has encroached closer and closer to the refinery. As of 2019, the Chilean environmental regulations have undergone a series of modifications that have tightened the allowable SO_2 emissions from the refinery and in particular the Fluid Catalytic Cracking (FCC) unit and the Sulfur Recovery Units (SRUs). This has resulted in closer scrutiny of the operation of the sulfur complex as a whole.

The refinery's sulfur complex consists of three amine systems, two sour water strippers and three SRUs (commonly called Unidades de Recuperación de Azufre, or URAs), two of which are Comprimo's EUROCLAUS® technology. In discussions with the government, the refinery has agreed to a certain daily SO_2 emission limit from the SRUs (and FCC unit), which requires the refinery to monitor throughput and unit operation more closely to stay within the new limits using Continuous Emissions Monitoring Systems (CEMS). For this reason, reliability of the units in the Sulfur Complex has become more of a concern to the refinery, especially as it was proving to be difficult to maintain the emission limits due to operational issues in the URAs.

ENAP engaged Comprimo to carry out an external technical review, which allowed a diagnosis of the system as a whole and makes it possible to define short, medium and long-term plans to ensure the reliability of the units, maintaining their availability and compliance with current environmental regulations.

The intent of this paper is to provide the learnings from flaws in the original design, operational miscues, operator misunderstandings, mismanagement of turnarounds, lack of maintenance, etc. This paper includes ENAP's intent of the technical review and expected outcomes while Comprimo describes the approach to this technical review and provides a summary of the findings that are being implemented to improve the reliability and availability of the units in question. The refinery's URA2, which proved to be the trouble child, went through a turnaround in Q2 of 2023; the results of the improvements are shared as well.

1.0 INTRODUCTION

The Aconcagua Refinery (ERA) is one of three refineries owned by the Empresa Nacional del Petróleo (ENAP). It has a processing capacity of 15,000 m^3/d of crude oil (100,000 BBL/d) distributed in two primary and vacuum distillation units. In its configuration, the refinery has different hydrotreaters, two Mild Hydrocracking (MHC) units, a Catalytic Cracking Unit (FCC) and a Delayed Coker Unit (DCU) among other process units.

The sour components produced in these units are processed in the following units:

- Sulfur Recovery Units 1, 2 and 3 (URA1, URA2 and URA3)
- Sour Water Stripper Units 1 and 2 (SWS1, SWS2)
- Amine Units (U500, U300, U950, U1700, U1800, U3000, U3200)

As of 2019, Chilean environmental regulations have undergone a series of modifications that have tightened the operation of the Sulfur Recovery Units and their associated units. In order to be able to monitor these emissions, CEMS have been installed in all three URAs.

Before these new regulations started, the allowable SO_2 emission was 2190 tonnes per year. However, since 2019, the regulations establish a decreasing limit with a target of 1145 tonnes per year for 2023 (a reduction of approximately 50%). In the chart below, the annual emissions limits are shown.

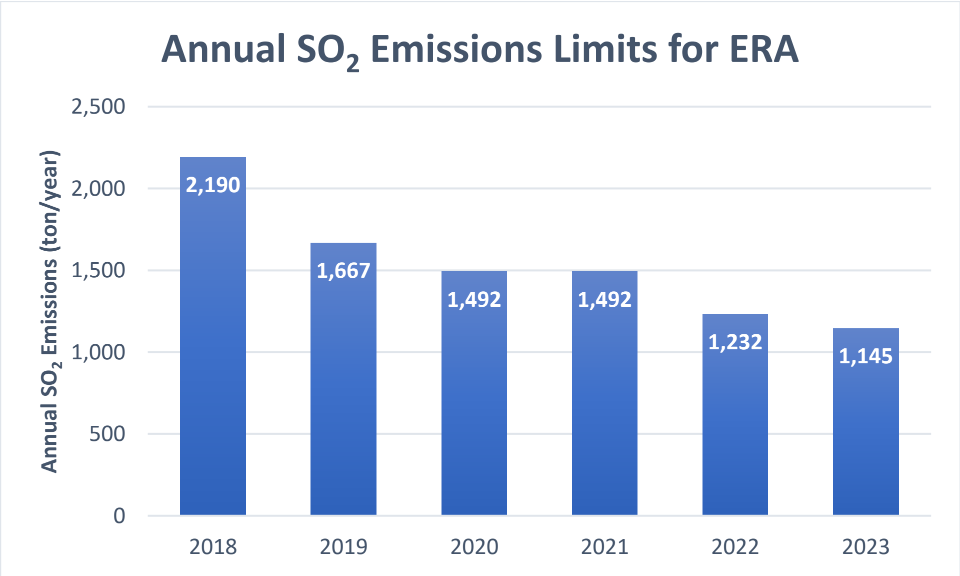

Figure 1. Aconcagua Allowable Emissions

Moreover, during 2020-2021, the availability of the sulfur treatment system had decreased considerably due to factors such as operational problems, load instability, maintenance shutdowns, early equipment and instrumentation failures, etc.

To investigate the causes of these increased emissions as well as the reduced availability of the units, ENAP contracted Comprimo, part of the Worley organization, to carry out an external technical review, which allowed a diagnosis of the system as a whole and made it possible to define short, medium and long-term plans to ensure the reliability of the units, maintaining their availability and compliance with current environmental regulations.

The technical review consisted of two one-week site visits, an operator questionnaire to evaluate the current knowledge of the design and operation of the units in question and a number of presentations and meetings to go over the past and current problems as well as the future projects to install a new sour water stripper and WSA unit.

Comprimo prepared worksheets for each individual unit as well as general worksheets that encompass multiple units to provide recommendations for physical and operational changes. The worksheets included which aspect of the plant is impacted by the worksheet as well as the severity of the current deficiency of the facility. The impact to the plant was segregated into the following categories:

- Efficiency = emissions
- Reliability = risk of failure of equipment or instrumentation
- Production = impact on total production of the refinery
- Safety = protection of personnel and public from harm

The severity of the worksheets was divided into the following categories:

- Critical – Consists of mitigation measures that must be implemented as soon as possible
- High – Consists of mitigation measures that must be implemented during the next plant shutdown in a planned manner
- Medium – It would improve the current performance, but mitigation measures are not fundamental to the plant's operations

A decision was made during the project to include cost estimates for the High and Critical items that were discovered. For worksheets that impact the production of the plant, ENAP and Comprimo agreed that any impact on refinery capacity would be indicated in the worksheet by Comprimo as increase or reduction in sulfur processing capacity and ENAP would determine what the revenue impact would be due to increase or reduction in processing capacity of the upstream hydrocarbon units.

2.0 PLANT DESCRIPTION

2.1 AMINE REGENERATION UNIT

There are three amine regeneration units in the refinery. ARU3200 services most of the absorbers in the refinery and uses DEA for the sweeting of the LPG and sour gas streams in primarily the Delayed Coker unit, Hydrotreaters and the Hydrocracker. Unit 1700 is a dedicated amine regeneration system for the Gasoline Hydrotreating Unit and uses DEA as well. Unit 570 is a dedicated amine system processing sour gas streams from the FCC unit using MDEA. Due to the relatively small impact of Units 1700 and 570 on the sulfur recovery units, the technical review only focussed on the ARU3200.

2.2 SOUR WATER STRIPPERS

Sour Water Stripper Unit 1500 (SWS1) consists of a modular, inside battery limits (ISBL) unit for the removal of H_2S and NH_3 from sour water streams originating in the FCCU, VHC, NHT and DHT units in the refinery. The SWS1 unit was designed by TPA in 1996 to process 42.7 m^3/h (188 GPM) of sour water to levels of 2 ppmw H_2S and 10 ppmw NH_3.

Sour Water Stripper Unit 3300 (SWS2) is an inside battery limits (ISBL) unit for the removal of H_2S and NH_3 from sour water streams originating in the Delayed Coker Unit (3000), the Naphtha / Distillate Hydrotreating Unit (3100), the Amine Regeneration Unit (3200) and the Flare (Unit 3740). The SWS2 unit was designed by Foster Wheeler in 2002 to process 44.6 m^3/h (196 GPM) of sour water to levels of 10 ppmw H_2S and 50 ppmw NH_3.

2.3 SULFUR RECOVERY UNITS

URA1 was designed by Advanced Petrogas Systems, initially with a capacity of 30 tpd and 96.5% sulfur recovery from amine acid gas (AAG) containing 82 mol % H_2S. Design was subsequently modified to also process a substantial amount of sour water acid gas (SWAG), while reducing the AAG based on maintaining original total air demand. SWAG accounted for 60% of total H_2S, reducing sulfur production capacity to 20 tpd. The unit was commissioned in 1994.

URA2 is a 2+1 EUROCLAUS unit designed by Comprimo in 2002 as a 2+1 SUPERCLAUS unit and converted to EUROCLAUS in 2016. The unit was designed with a capacity of 45 tpd and 99.1% sulfur recovery, processing Amine Acid Gas with an H_2S content of 82 mol% and Sour Water Acid Gas containing 25 mol% H_2S and 25 mol% NH_3.

URA3 is a 3+1 EUROCLAUS unit designed by Comprimo in 2006. The unit was designed with a capacity of 45 tpd and 99.3% sulfur recovery, processing Amine Acid Gas with an H_2S content of 90 mol% and Sour Water Acid Gas containing 28 mol% H_2S and 38 mol% NH_3.

3.0 TECHNICAL REVIEW

3.1 FIELD REVIEW

The first step in the review of the units in the Sulfur Complex was to walk through the plant to determine whether there were any initial indicators of potential issues with the units during operation. This also included discussions with operations about operating modes that could lead to potential problems with emissions.

3.1.1 URA2 and URA3 Sulfur Pit Vent Plugging

The sulfur pits T-1641 and T-3501 in URA2 and URA3 have the Shell Sulfur Degasification technology installed. The vent gas systems from both Sulfur Pits are plugged and there is evidence of a leak on the sweep air intake line in URA2.

Figure 2. URA3 Sulfur Pit

Figure 3. Vent air escaping from the access hatches in URA3 Sulfur Pit

Figure 4. Vent air escaping from sweep air intake (left)/ leaking elbow on sweep air intake (right)

As the stripping air flow to the sulfur pits bubble columns has not been stopped and the vent gas piping to the Thermal Incinerator was plugged, the vent air containing H_2S and SO_2 is released via the man access hatches in URA3 and the sweep air intakes in URA2. This is creating a situation with continuous release of H_2S to the atmosphere in excess of the maximum allowable concentration (MAC) of 10 ppmw. As a result, the areas around the sulfur pits are not safe and Comprimo recommended to take action to minimize access to these areas.

With the inability to sweep the sulfur pit vapour space, Comprimo does not believe it possible to stop the degasification of the sulfur due to the risk of creating an explosive mixture in the vapour space of the pits.

3.1.2 Plant Heating

Plant heating appears to be a major concern in the facility. The following systems are considered critical to be properly heat maintained:

- Sour water acid gas - maintain wall temperature and all instruments above 75°C (167°F)
- Sulfur lines – maintain wall temperatures and all instruments above 125°C (257°F)
- Vapour lines containing sulfur – maintain wall temperatures and all instruments above 125°C (257°F)
    - Only applies for systems with normal temperatures below 140°C (284°F) and systems that can have stagnant flow

The heat maintenance of a system heavily depends on the following four factors:

- Type of tracing
    - Tube tracing
    - Bolt-on jacketing
    - Jacketing
- Pressure and quality of the steam supplied to the tracing
- Type and maintenance of the steam traps installed
- Condensate back pressure

A portion of the sour water acid gas lines as well as the vapour lines containing sulfur appear to be traced with ¾" or 1" pipe tracers, which depending on the line size may have 2-6 tracers with often sections of insulation missing or no insulation at all on flanges. Most of these tracers did not touch the piping to provide direct conductivity of heat from the tracer to the pipe wall. Most of the interconnecting sour water acid gas piping between the sour water strippers and SRUs was jacketed, however due to failed welds, the plant no longer kept the acid gas piping hot, resulting in substantial corrosion in the interconnecting piping.

Figure 5. URA2 Tail gas piping tracing.

Figure 6. Sour water acid gas piping tracing.

Figure 7. Tracing of vent gas piping including unheated pipe support.

Flanges in these services act like very large heat sinks and must be traced as well. In practice it is not possible to get good contact between a tracer and the flange, and it is therefore recommended to install bolt-on jackets onto the flanges, which must be insulated. There were several examples found in the plant where these were installed, however the majority of the flanges in sour water acid gas and sulfur vapour service were found to be exposed to the atmospheric conditions.

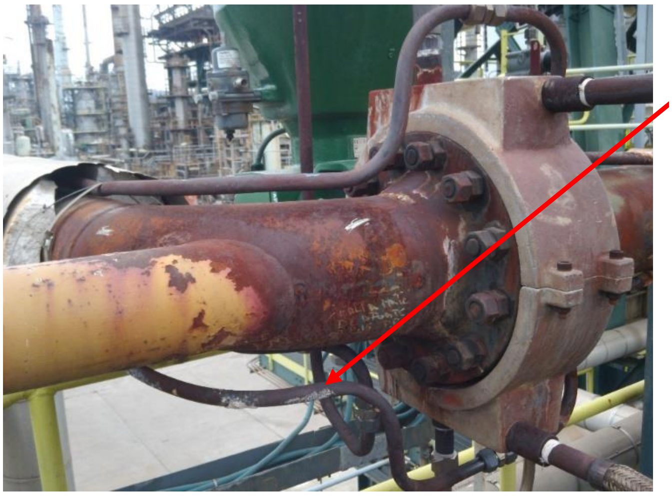

Figure 8. Bolt-on jacketing for flanges.

Note in Figure **8** that the 1” pipe tracer does not touch the pipe, which makes the heating very inefficient and this vent line from the pit is likely plugged with solid sulfur.

In the case of sulfur rundown lines, there appears to be a problem with the trap selection and the condensate return system. During the review, a freezing of one of the Sultraps in URA1 was observed first-hand with the event resulting in a substantial safety risk to the operators as well as a spill of sulfur to grade.

Figure 9. Consequences of frozen Sultrap in URA1.

Note in the second image the installation of the steam trap, which appears to be a thermostatic type with a ¼” condensate return line with a severe bend at the outlet of the trap. As thermostatic traps operate on the basis of temperature difference, the condensate has to be subcooled before the trap opens, which will result in potential temperatures below the freezing point of sulfur. By removing the trap all together, the steam could flow continuously through the jacket resulting in the melting of the sulfur in the Sultrap. This is not a good practice and it was recommended to ENAP to do a full review of the steam and condensate systems for the heat maintenance in the sulfur recovery units.

3.1.3 Sulfur Rundowns – F-1643A/B/C/D/E

The sulfur rundown lines have “sulfur boots” installed. These sulfur boots are supposed to remove any debris from the rundown system, before it can reach the sulfur seals/locks.

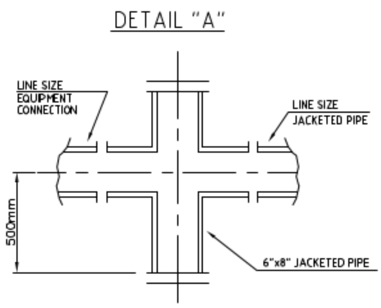

Figure 10 - Sulfur Boot Design Detail

Per the sketch in Detail “A” the inlet nozzle and outlet nozzle from the boot should be installed at the same elevation to allow rodding of the rundown piping through the boot, sulfur rundown valve and outlet nozzle of the condenser

In URA2, it appears that several of the sulfur boots were modified to meet the slope of the rundown lines per the design requirements (1 degree slope), resulting in the inability to rod the entire sulfur rundown line into the condenser. Figure **11** shows the rundown sulfur boot for the third condenser.

Figure 11 - Sulfur Boot on Third Condenser

3.2 OPERATIONAL REVIEW

3.2.1 Adverse Conditions Operation

The ground level SO_2 concentrations near the refinery can be impacted by certain weather conditions. As a result, an operational plan for the Aconcagua Refinery was agreed upon with the Environment SEREMI (local regulators), as part of the Plan de Prevención y Descontaminación Atmosférica (PPDA). This included as mitigating strategy that the refinery cut back its capacity in four of its units including the processing of sour water in Sour Water Strippers SWS1 and SWS2 during a scenario defined as Adverse Conditions. This leads to short term reduction of the emissions from the refinery, however it does create upset situations in the URAs. Every time the sour water stripper capacity is reduced, a lower SWS acid gas load is introduced to the URAs resulting in a tail gas upset and temporary increase in SO_2 emissions. The same occurs at the end of the Adverse Conditions, when the SWS capacity is increased again.

Comprimo evaluated the impact of the Adverse Conditions and there is an overall negative impact on the emissions from the refinery due to the shift in load of SWS acid gas from high to low flows. Ammonia has a detrimental effect on emissions due to the dilution effect that it creates during an increase in sour water acid gas processing after the completion of the Adverse Condition upstream of the SUPERCLAUS reactor. As such the URA2 and URA3 lose sulfur recovery efficiency which is not recovered during the Adverse Condition operation, when the sour water acid gas rates are reduced. As a result, the average emissions between operating with or without Adverse Conditions, are higher due to the negative impact that increasing the sour water acid gas flow rate has on the performance of the EUROCLAUS unit.

Another observation involves the feed forward portion of the Advanced Burner Control (ABC) System. The feed forward portion normally consists of using air to amine acid gas and air to SWAG ratios to determine the theoretical air demand (in addition to the air to natural gas ratios in case of co-firing). Over time the operators had adjusted the two air to acid gas ratios to manage upset situations in the SRU, which had resulted in the two ratios being substantially removed from the original design values. With the Adverse Conditions Operation and the twice daily changes in sour water acid gas due to load reduction, a substantial impact was seen during these times in emissions due to incorrect calculation of air demand as a result of the incorrect air to SWAG ratio. Especially with plants that have a substantial swing in acid gas flow rates, it is essential to ensure the air to acid gas ratios are as accurate as possible.

3.2.2 Load Distribution

One of the observations of the refinery's operation of the sulfur recovery units was how the load was distributed between the three URAs. The plant had a practice of operating URA1 with minimum load or on hot standby, URA2 in flow control and URA3 in pressure control on the amine and sour water acid gas. As URA3 was designed as a 3+1 EUROCLAUS unit with the highest sulfur recovery efficiency, this appeared to be not the optimum solution for the lowest emissions for the sulfur complex. Especially with URA2 underperforming, this appeared to result in even higher emissions.

Comprimo recommended to change the operation to maximizing the load on URA3 in flow control and operating URA2 as the swing unit with the amine and sour water acid gas in pressure control, thereby using the highest recovery of URA3 to the benefit of minimizing the emissions.

3.2.3 URA2 operation

URA2 appears to have been the problem child of the refinery for a number of years now with respect to emissions. Due to agreements with the government, the EUROCLAUS® Selective Oxidation catalyst was replaced in this unit every six months for several years. This also meant that every six months the fresh catalyst needed to be conditioned, which is period of higher emissions for the refinery. During the conditioning, URA2 operates at reduced sulfur recovery efficiency, requires operation with only amine acid gas for about 5-7 days and requires full attention of the board operators to monitor the progress of the conditioning.

A review of the 2020 conditioning of the EUROCLAUS® Selective Oxidation catalyst demonstrated that there is a lack of knowledge of the required operation during the conditioning of the catalyst. In Figure 12 below, the DCS trends from the 2020 conditioning step are provided and it appears that the oxidation air (in red) was not maximized during the initial phases of the conditioning.

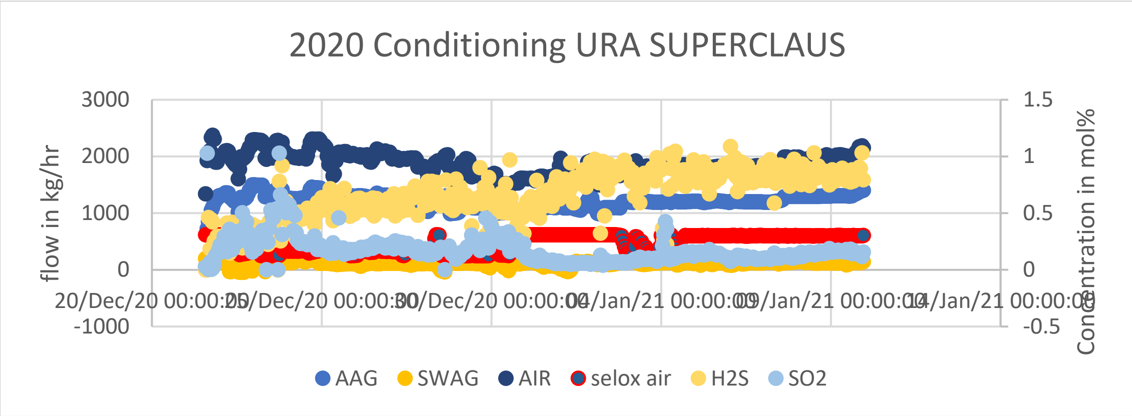

Figure 12. DCS trends from EUROCLAUS Selective Oxidation Catalyst Conditioning Step

Upon review of the operating conditions as well as the results from samples taken downstream of the coalescer during the first site visit in May 2022, it was found that the typical emissions from the stack of URA2 were in the order of 2500 ppm SO_2 and that the yield of the EUROCLAUS® Selective Oxidation catalyst was below 70% which is an indication of deactivation of the catalyst.

In Figure 13, the DCS trends between May 24th 2022 and June 6th 2022 are provided for the third (EUROCLAUS® Selective Oxidation) reactor temperature (bottom) as well as the period around a plant trip over a 6 hour period (top).

- Top left corner (6 hour period):
  - Blue = sour water acid gas flow
  - Green = amine acid gas flow
  - Yellow = stack SO_2
- Top right corner (6 hour period)
  - Green = excess O_2
  - Blue = oxidation air flow
  - Yellow = Third reactor inlet temperature
- Bottom left corner (April 24 – June 6)
  - Green = Third reactor top temperature (right side)
  - Blue = Third reactor top temperature (left side)
  - Yellow = Third reactor middle temperature (left side)
- Bottom right corner (April 24 – June 6)
  - Green = Third reactor middle temperature (right side)
  - Blue = Third reactor bottom temperature (left side)
  - Yellow = Third reactor bottom temperature (right side)

There are two items that stand out in these trends that merit further discussion:

1. There appears to be a preferential temperature rise on one side of the third reactor as well as a temperature drop in the bottom of the reactor on one side. For instance, on June 6th, the temperatures in the reactor were as follows:

	Left	**Right**

Top	199.6 °C	225.2 °C
Middle	267.4 °C	300.3 °C
Bottom	275.3 °C	292.0 °C

This is not normal for a Selective Oxidation reactor as the temperature rise is always steady from top to bottom. And with a properly installed and conditioned catalyst, there should be little difference in temperature profile between the two sides of the reactor.

2. On May 4th 2022, URA2 experienced a trip of the unit caused by a low low amine acid gas flow. The interesting observation from the unit trip was that after the unit was returned to normal operation, the severe preferential temperature rise on the right side of the reactor was no longer there and it appeared that the temperature rise occurred equally on both sides of the reactor.

	Left	**Right**
Top	195 °C	195 °C
Middle	245 °C	260 °C
Bottom	270 °C	270 °C

At the same time, the emissions from URA2 dropped from over 2000 ppm to less than 1500 ppm, showing a dramatic improvement of the performance of the third reactor. During the trip, the blowers also tripped, resulting in the absence of air to the reactor while the reactor was in bypass operation.

This improvement in performance was not sustained and after about 10 days, the temperature difference between the left and right side started to occur again with the situation getting progressively worse. In the month after the URA2 trip, the bottom temperature rose from about 270°C to 300°C, consistent with a decrease in selectivity of the catalyst. In addition, it appeared that the temperature in the middle right side of the reactor was higher again than the bottom right side.

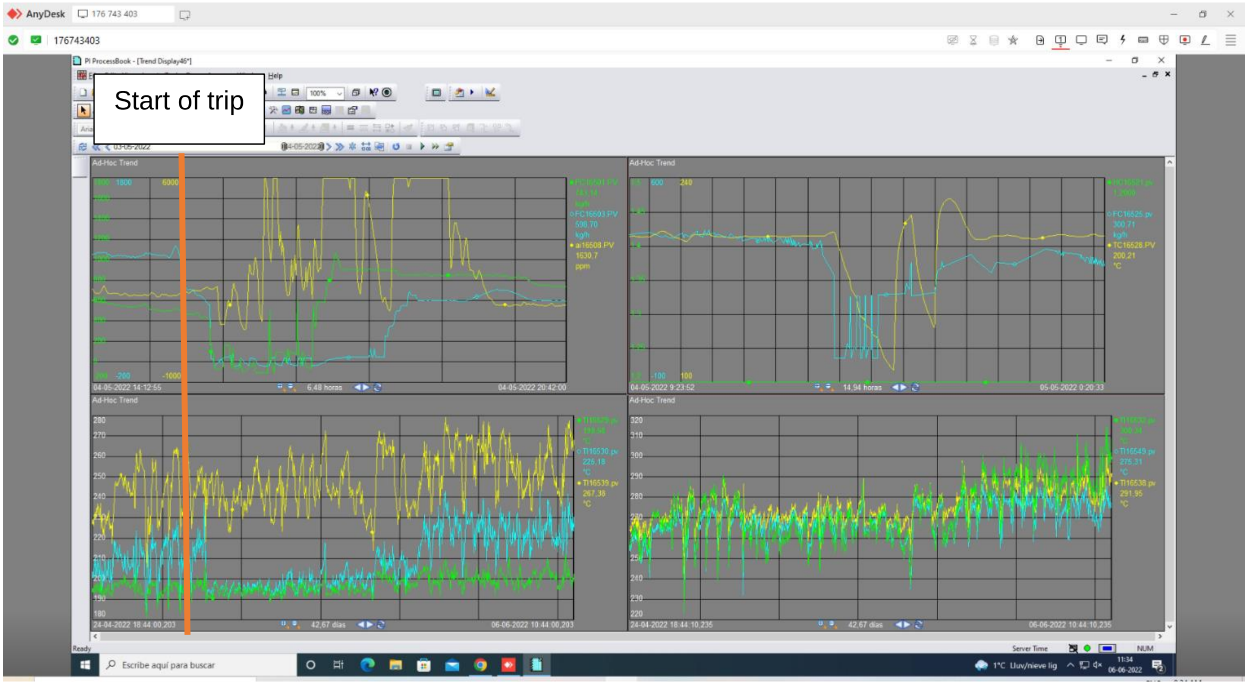

Figure 13. DCS Indication of Low Low Amine Acid Gas Flow Trip in URA2

Figure 14 shows the same trends as Figure 13 for the entire period from April 24th until June 6th. In the past, the plant had used an increase in excess oxygen to solve the problem with the temperature differential between the two sides of the reactor. To try to correct the temperature differential, the excess oxygen was increased from 1.2% to 1.5%, however this did not have the desired effect. It appeared to increase the bottom temperature more and slightly increase the SO_2 emissions from the stack.

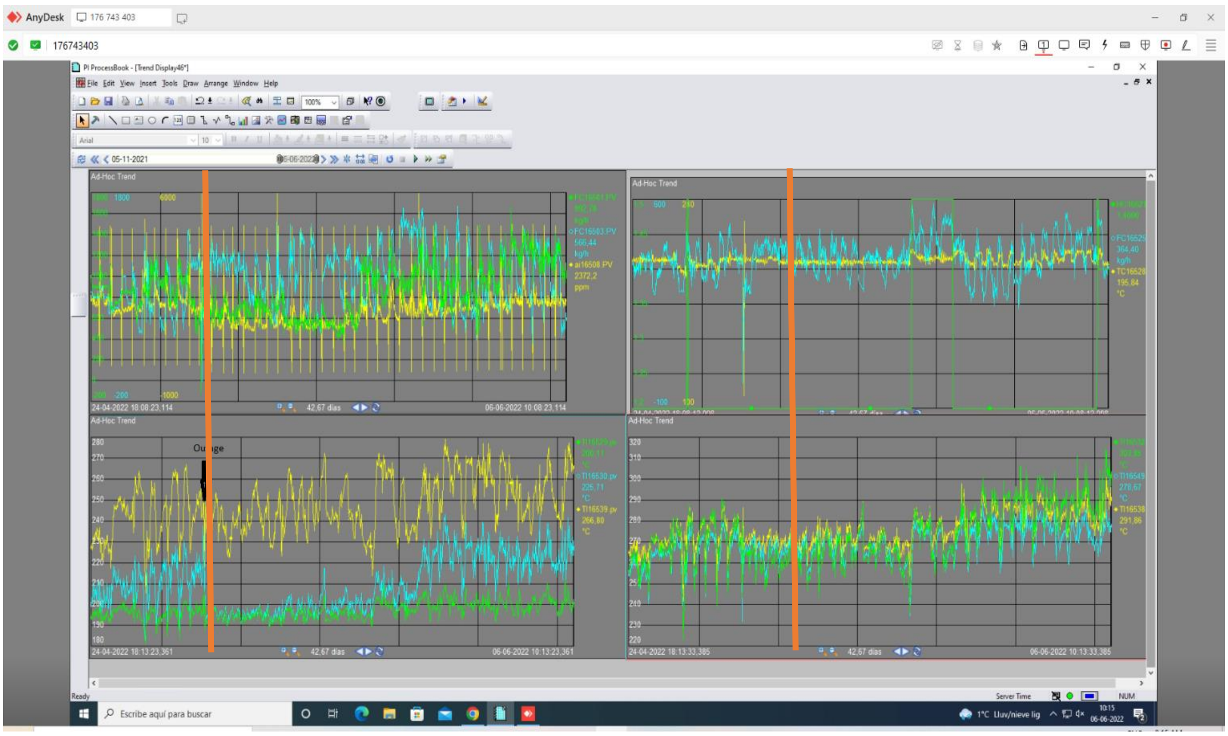

Figure 14. DCS Indication of SWAG and AAG Flows, Stack SO_2 and third reactor Parameters for URA2 (April 24th to June 6th, 2022)

Several other items were observed at that time:

- Comprimo observed that the sulfur flow from the third sulfur condenser C-1644 was lower than the sulfur flow from the fourth sulfur condenser C-1645,
    - This is unusual as the sulfur production decreases as the process progresses.
- The sulfur rundown including the sulfur boot from the third condenser C-1644 were opened and checked for plugging and no evidence of plugging was observed in the rundown piping.
- A sulfur flush was performed, which did not appear to improve the sulfur flow.
- There was sulfur coming out of the demister box on C-1644. See also Figure 15.

Figure 15. Evidence of sulfur from the demister box in URA2 Third Condenser C-1644

Based on all the evidence above, Comprimo had strong suspicions that the poor performance of the catalyst in the URA2 third reactor D-1643 is caused by continuous sulfur carryover from the third condenser C-1644. As the rundown appeared to be open, Comprimo suspects that the sulfur carryover is caused by a partial blockage of the sulfur outlet nozzle in the outlet channel of C-1644, likely caused by a collapsed demister. Surprisingly the Inspection Report RS-GC-IF-04 from 09-07-2021 does not show any indication of issues with the demister, so the problem could also be caused by a partial blockage in the sulfur rundown isolation valve.

The effect of sulfur carrying over to the third reactor D-1643 is that on one side of the catalyst, the sulfur blocks the active sites of the catalyst, and the sulfur continuously flows slowly down the catalyst. As a result, there is poor behaviour of the catalyst and also potentially some Claus activity across the catalyst due to the presence of liquid sulfur. Due to the heat of vaporization of the liquid sulfur flowing down the catalyst, it is possible for a temperature decrease in the bottom of the reactor as was observed. In addition, the sulfur carryover also explains the higher sulfur flow from the fourth sulfur seal F-1643D compared to the flow from the third seal F-1643C.

3.2.4 ARU Fouling

The refinery indicated that in the latest turnaround approximately 17 barrels of sludge were removed from the Amine Flash Drum F-3201. This was the first time since the initial start-up in 2008 of the unit that the Amine Flash Drum had been cleaned. In addition, the refinery was shutting down ARU3200 every three months to clean the trays with indication that the lean/rich exchanger C-3201 was fouling rapidly as well. There was evidence of foaming in the Amine Regenerator E-3201 on a regular basis.

The current practice of the refinery is to filter 10% of the rich solution from the Amine Flash Drum F-3201 to the Amine Regenerator C-3201 in the Rich Amine Filter L-3205. Approximately 30% of the lean amine is filtered in the Amine Solution Filter L-3201, after which the amine is passed through the Amine Carbon Filter L-3202 and the Amine Particulate Filter L-3203. Per refinery information, the rich filter elements are changed once a week and the lean amine filter elements are changed every 2-3 weeks.

Comprimo inspected the amine stored in the Amine Surge/Storage Tank T-3201 and found the amine to be very dirty, even though operations indicated that the lean amine in the circulation is very clean as demonstrated in Figure 16.

Figure 16. Amine samples from Amine Surge/Storage Tank (left) and lean amine sample (right)

Upon further investigation, Comprimo observed that the Amine Surge/Storage Tank T-3201 was designed with the inlet and outlet nozzle located on the same side of the tank (see Figure 17) and hence Comprimo suspects that the lean amine is shortcutting through the tank. It is suspected that a substantial layer of sludge has built up in the tank.

Figure 17. Amine Surge/Storage Tank inlet and outlet nozzle

3.2.5 Sour Water Tank Skimming Issues

Hydrocarbon separation from sour water is an essential component in the reliable operation of sour water strippers. At the Aconcagua refinery, there are two sour water tanks installed as part of SWS1 and SWS2, however T-1501 is currently not in operation and there is evidence that there are issues with the floating roof as well as the installed oil skimmer in T-3301, resulting in an inability to remove the hydrocarbon from the tanks. Per indication from the refinery, T-3301 currently contains about 65% hydrocarbon with no ability to remove this hydrocarbon.

Several upsets were experienced during Comprimo's presence at the refinery that were caused by hydrocarbon carry-over with the sour water to the sour water strippers, which resulted in very high emissions from the SRUs. In addition, there appear to be continuous issues in the SWSs and the URAs due to the presence of hydrocarbons in the feed to the SWSs, which include the regular requirement to clean the URA3 SWS gas KO Drum F-3502 and the inability to control the overhead temperature in SWS2.

There is currently project planned to implement a water wash on the SWS Gas KO Drum in URA3. This will potentially solve the consequences of the hydrocarbon carryover events, but not be the permanent solution. Comprimo recommended first of all to fix the issues with the tank skimmer however also recommended installing a hydrocyclone or liquid/liquid coalescing filter upstream of the sour water stripper to provide enhanced oil recovery from the sour water feed.

3.3 DESIGN REVIEW

3.3.1 SWS2 – Overhead Condenser C-3303

The Overhead Condenser C-3303 in SWS2 is a unique Alfa Laval spiral exchanger comprised of concentric vertical parallel plates. Cooling is provided by flow of a sour water slipstream between alternate plates, entering at nozzle B1 in sketch and leaving via B2. Stripper overhead vapours pass upward through the centre, then downward between alternate plates. Gas and liquid separate within an outlet channel of sorts at the bottom of the exchanger. Liquid drains via low-point 2" nozzle A2, and gas exits via higher 3" nozzle A3. Reflux gravitates from A2 to the top Stripper tray via a liquid seal to prevent counterflow of bypassing gas.

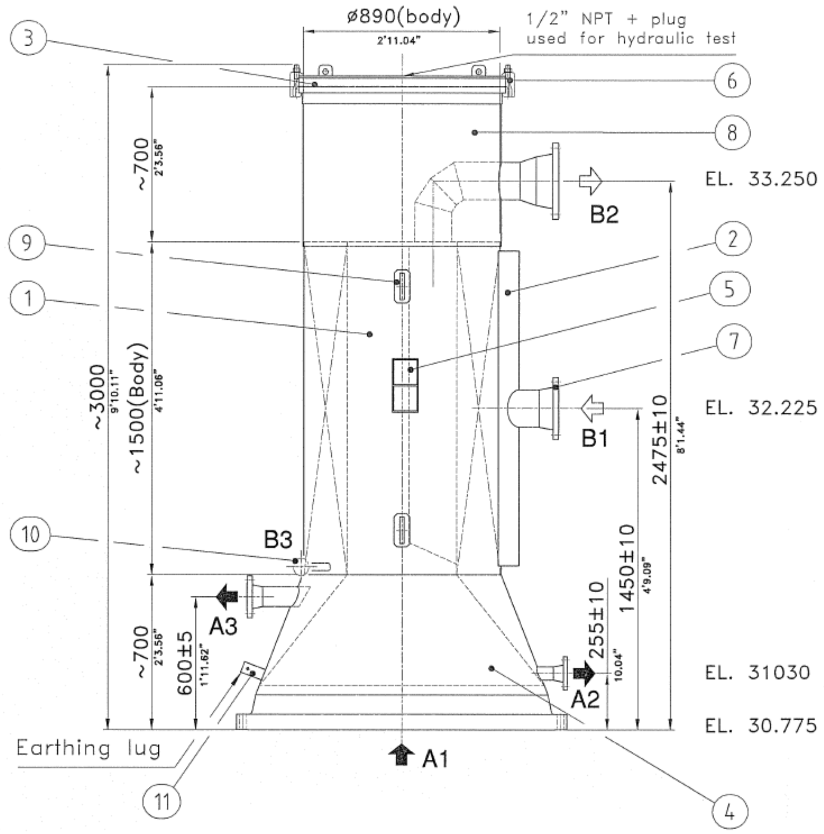

Figure 18. SWS2 Overhead Condenser C-3303

The plant has had substantial issues controlling the overhead temperature of the sour water stripper with this exchanger and due to instabilities is currently operating the temperature control in MANUAL.

In principle, Comprimo believes that this exchanger should be able to perform as original intended, however it is Comprimo's belief that because there are severe issues with hydrocarbon carry-over, there is a great potential for foaming and fouling of this exchanger which creates pressure differential issues that result in instabilities in the control. A dip-leg is used to create a pressure break for the reflux water back to the tower. In the scenarios where the pressure drop across the exchanger increases beyond the hydraulic depth of the dipleg, it is possible to create situation with intermittent gas blow through the dip-leg.

The main issue that was identified with respect to the hydrocarbon carry over was a problem with the skimmer in one of the sour water tanks that could not be corrected due to inability to shut down one of the sour water tanks as well as an inability in the refinery to reprocess large amounts of slop oil.

3.3.2 ARU3200 – Absence of Flash Gas Contactor

The Amine Flash Drum F-3201 is not installed with an amine flash gas contactor, which is unusual for an amine system. In a typical design, the flash gases, which contain H_2S and CO_2, are recontacted with a small packed contactor installed on the top of the Amine Flash Drum. After the removal of the H_2S and CO_2, the gas is then reused as fuel gas in the overall fuel gas system or as supplemental fuel gas in the Thermal Oxidizer. In the current configuration, the flash gases are routed to the Flare, where it results in additional SO_2 emissions as well as a loss in fuel gas. Currently there is no government mandate to reduce the SO_2 emissions from the Flare stack, so the operation of this system can be retained as is.

3.3.3 ARU3200 Overhead Condenser bypass

It is Comprimo's understanding that a bypass was added around the ARU3200 Overhead Condenser C-3203 to prevent overcooling of the process gases from the regenerator. Comprimo believes that this is not required and there is no concern to operate the overhead temperature of the regenerator as cold as 30°C during colder days by just operating the air cooler. In addition, ENAP has observed an increase in corrosion in the air cooler, which is likely caused by the additional deposit of ammonium bisulphide in the inlet of the tubes due to the reduction in washing as part of the condensation.

3.3.4 URA2/3 – Sour Water Propulsion Vessel

The original design provided by Comprimo for URA2 and URA3 included the installation of a propulsion vessel (F-1645/F-3505) to remove the sour water collected in the amine gas KO drums and SWS gas KO drums. The drums work on the principle that the liquid in each drum is manually moved to the propulsion vessel when a level is observed in the KO drum. Once the liquid is moved, the vessel is isolated from the process and pressured using nitrogen to the sour water system for reprocessing.

In practice, it appears that this system does not work well due to leaking nitrogen valves resulting in a continuous higher pressure in the propulsion vessel than the KO Drums and an inability to drain the water from the KO drums.

ENAP has already added connections from both acid gas KO drum (F-1602) in URA2 to the KO Drum pumps in URA1 (J-1102A/B). These lines are long and appear to be in a very corrosive environment (in standing water) and are at risk to fail in a short time.

3.3.5 Blower Types in URA1 and URA3

In URA1 and URA3 reciprocating air blowers have been installed. This is a rather uncommon occurrence as per Comprimo's experience all blower in combustion air service are centrifugal blowers.

In URA1, the original two blowers were centrifugal style blowers, however after failure of one of the two blowers a replacement rotary positive displacement blower was installed. Since that installation, ENAP has not been able to switch the blowers online anymore due to the different behaviour of the two types of blowers. A centrifugal blower follows a curve and requires a blow off system to protect against surging, whereas a positive displacement blower requires control of the discharge pressure via speed control of the motor and a pressure regulating valve to atmosphere.

In URA3, both blowers are reciprocating and Comprimo observed that switching blowers can be rather difficult due to the pressure control of each blower. If it is not done slowly, it is possible to trip the URA on low air flow, which happened on June 18th 2022.

In addition, the control of the blowers in URA3 is currently set up with continuous full blow off of the air via the pressure regulating valve, with no apparent control of the header pressure using the speed control of the blower. Comprimo has provided a recommendation for the modifications to the URA3 blower controls to control the header pressure, while reducing the power consumption.

3.4 EQUIPMENT INTEGRITY

One of the items that has plagued the plant in the last couple of years is premature failure of equipment, leading to a number of unplanned outages of the URAs and SWSs.

3.4.1 Failure mechanisms

The following items were described as causing issues in the refinery:

- Plugging of gas piping containing sulfur vapour
- Leaking piping processing gas containing sulfur vapour
- Leaking tubes in sulfur plant waste heat boilers and condensers
- Leaking tubes in sulfur plant (P)reheaters
- Plugging and corrosion in SWS1 pumparound system
- Corrosion in the ARU overhead condenser
- Indication of loss of material in the URA tail gas piping due to corrosion

In general, all of the issues described above can be brought back to two issues:

- Insufficient heating
- Incorrect material of construction

For lines containing sulfur (including the waste heat boiler and condensers), heat maintenance is essential to ensure that the sulfur remains in the gaseous or perhaps even the liquid form. When the piping is below 120°C, sulfur will freeze on the walls of the piping and equipment, which can lead to something called wet sulfur corrosion. This process is very aggressive in carbon steel and has been investigated in depth by Alberta Sulphur Research Ltd. (ASRL). In their research on the corrosion mechanism of carbon steel, they found values as high as 120 MPY for corrosion rates with wet sulfur in the piping. Therefore, it is essential to ensure that all piping, flanges and instrumentation are properly heated and insulated, maintaining a wall temperature above 120°C, to prevent deposition of sulfur in the presence of liquid water. Regular tube tracing is inadequate to maintain the wall temperatures and in the case of ENAP the flanges were not included in the tracing, leading to cold spots in the systems where there are bare flanges. It is therefore recommended to replace all systems that are currently installed with tube tracing with ControTracing, which has proven to be much more reliable to maintain the wall temperatures of the piping and equipment in service with sulfur vapour.

For vapour lines containing ammonia and H_2S, it is essential to maintain the temperature of the piping above about 70°C. Below this temperature it is possible to sublimate ammonium bisulphide crystals which in the presence of water can lead to very high concentration of ammonium bisulphide, which will collect in low points as well as instrument connections. Typically, when ammonium bisulphide is present in the piping, weaker spots such as elbows are prone to leaks. Similar to the recommendation for systems containing sulfur vapour, it is essential to maintain the wall temperature of sour water acid gas piping at temperatures above 70°C, which is very difficult with regular tube tracing. It is Comprimo's understanding that there are fully jacketed systems installed in the refinery, however that a number of these jackets have failed, resulting in no heating at all currently. Again, ControTracing is recommended for all sour water acid gas systems to ensure that the corrosion in these systems can be minimized.

As for the corrosion in the pumparound system, this appears to be pure and alone a matter of incorrect metallurgy. The concentration of ammonium bisulphide in a sour water stripper pumparound system typically exceeds values of 6-8 wt%, at which point stainless steel is required. The pumparound system in SWS1 is fully made from carbon steel, so this is likely the main reason for the high corrosion rates, issues with the isolation valves and leaks on the pumps. Comprimo believes that if the metallurgy of the system is not upgraded (pumps, piping, isolation valves, air cooler tube material and control valve) from carbon steel to stainless steel, the system will remain to be problematic and continued preliminary failure can be expected.

The overhead system of SWS2 consists of a reflux condenser (albeit an unusual one) and it is our understanding that the sour water processed in this unit contains hydrogen cyanide. Hydrogen cyanide is known in our industry to increase the corrosion rates in condensing service systems in the presence of ammonium bisulphide and it is therefore likely the cause for the higher corrosion rates that are observed in the reflux line from the overhead condenser. This system is currently fabricated from stainless steel, however in the presence of hydrogen cyanide it is not unusual to see failures of the piping system downstream of the overhead condensers within three months due to the high corrosion rates. Industry practice has been to use titanium for the tubes and the piping between the condenser and the reflux drum. More recently, higher alloy metals such as duplex 2205 have been considered and installed with mixed success. Therefore, as a minimum a higher-grade metal shall be used to replace the reflux line from the condenser back to the tower.

3.4.2 Preventive Maintenance

A sulfur recovery unit is prone to failures when the unit is started-up or shut-down. During normal operation, most of the equipment is hot and there is typically little cause for concern in the unit. The typical causes of failure are very often related to the presence of wet elemental sulfur (which is normally tied to incorrect start-up and shutdown procedures as well as insufficient heating). In addition, poor quality of boiler feed water and insufficient blowdown of the waste heat boiler and condensers can lead to early failure of the system.

It is therefore essential that proper operating procedures to maintain good boiler feed water quality in the waste heat boiler and condensers are in place. In the Waste Heat Boiler, the intermittent blowdown shall be opened once a shift for about 30 seconds to remove any built-up sludge in the exchanger. The continuous blowdown on the WHB shall be set up to maintain the pH of the water in the boiler between 7 and 9. The required pH and conductivity for the boiler feed water in the WHB and Condensers is provided in Table 1.

In addition, all heating systems shall be inspected using a piece of sulfur to determine whether the steam supply system and condensate traps are operational for piping and equipment that contain sulfur or ammonium bisulphide.

The best preventative maintenance in a sulfur recovery unit is to minimize the number of start-ups and shutdowns. If there is a requirement to reduce the acid gas flow to one of the units for an extended period, the unit can be put in hot standby for an undefined period as long as the main burner is operated without forming soot. This could mean after a heat soak and sulfur burn, operation with excess air or without a heat soak and sulfur burn, operation at 90-95% stoichiometry and introduction of LP steam for flame moderation.

For the amine system, the key preventative maintenance activity is to manage the health of the amine solution in circulation. This can be done using the amine filters installed in the plant as well as the activated carbon bed. The pressure drop across the particulate filters shall be monitored and the filter elements shall be replaced when the pressure drop exceeds the vendor recommended value. The activated carbon bed shall be monitored for foaming tendency downstream of the bed. The currently indicated replacement of the amine particulate filters and activated carbon appears to be in line with industry practices. Comprimo does recommend moving to a full flow rich filter to further enhance the health of the amine solution.

Additionally for the amine system, monitoring of the heat stable salt concentration is essential and if the heat stable salts exceed the vendor recommended values, the amine shall be cleaned by a specialized company using ion-exchange.

Proper planning of turnaround cleaning of the Amine Flash Drum and Amine Regenerator needs to be done to ensure that problems (scale, iron sulphide) do not accumulate in the stagnant areas of the plant. This includes the Amine Surge/Storage Tank as well.

There are not a lot of preventative maintenance activities that can be considered for the sour water strippers, except the maintenance of the hydrocarbon level in the sour water tanks. Hydrocarbon separation is the key to any sour water stripper and proper monitoring and skimming of the hydrocarbons is essential to maintain clean equipment in the sour water strippers.

In the case of Aconcagua, Comprimo does recommend additional monitoring of the metallurgy losses in the pumparound of SWS1 due to the inadequate carbon steel metallurgy.

3.5 CONTROL SYSTEM REVIEW

3.5.1 Blower Controls

The URAs use a combination of centrifugal and reciprocating blowers for the supply of air to the main burner, SUPERCLAUS® and Sulfur Degassing. The use of positive displacement blowers is not usual for sulfur recovery units and Comprimo has more experience with the use of Centrifugal Blowers instead.

In order to minimize the power consumption of combustion air blowers, the vent valve should only be used to protect the operation of the blower. In the case of a positive displacement blower this means that the system should be set up such that the combustion air header pressure is controlled by modulating the speed of the motor or the opening of the governor of the steam turbine and only when the speed has reached the minimum speed, the vent valve shall be opened to release the excess air from the blower to atmosphere.

In URA3, the blowers operate always with maximum speed with no control from the combustion air header pressure controller and the vent air controlling the header pressure through the pressure regulating valve. In essence the header is controlled pure and alone through the venting of air, meaning that a substantial higher power consumption is use than is necessary.

3.5.2 SWS2 overhead temperature control

The overhead temperature control of SWS2 has not worked in AUTO since the unit was installed. The control is supposed to use a three-way valve to bypass sour water feed around the reflux condenser. Per discussions with the operators, it appears that this control is not stable in AUTO and the opening of the three-way valve is adjusted manually as a function of the processing capacity of the unit. A snapshot of the control is provided in

Figure **19** below.

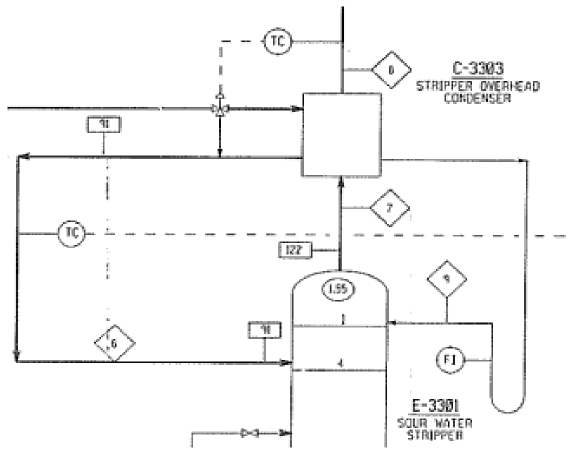

Figure 19. SWS1 overhead temperature control.

In theory, this control should work properly. The SWS acid gas temperature is cooled by the amount of water sent to the reflux cooler and the amount of reflux is routed through the dipleg back to the column. In practice it is found that the flow measurement of the reflux in FI-33009 is not reliable and that there is severe instability in the operation of the system with substantial risk of liquid carry over to the URAs. One item to note is that the Process Flow Diagram has the flow element downstream of the dipleg, whereas it is located in the inlet side of the dipleg instead on the P&ID and in the field. By placing this flow measurement in the upstream side of the dipleg, the flow measurement is dependent on the presence of liquid in this line, which may not always be the case upstream of the dipleg.

Comprimo suspects that due to the carry-over of hydrocarbons, there is a substantial risk of foaming and fouling of the heat exchanger, resulting in improper operation of the dipleg and regular pressure drop issues across the exchanger. If the pressure drop across the exchanger is higher than the dipleg, it is possible for incorrect flow direction in the exchanger and a high carry over of liquid with the SWS acid gas.

Based on observations of the operation of the SWS2, the feed to this unit appears to be relatively constant, with the exception of the change between normal and adverse conditions. Therefore, Comprimo believes that there is little need to have automatic control in this unit until the issues with hydrocarbon carryover have been resolved through the repair of the oil skimmers in the sour water tanks and the installation of enhanced hydrocarbon removal technologies in the feed to the sour water strippers. Once the hydrocarbon issues are resolved and the overhead exchanger has been cleaned and maintained, the controller can be re-established in AUTO control to determine whether this has improved the operation.

3.5.3 Maintenance of Air to Acid Gas Ratios

The ABC control system uses a manually set air to acid gas ratio for both the amine acid gas and the sour water acid gas. These values are used to determine the theoretical air demand of each URA on the basis of the measured amine and SWS acid gas flow rates. In addition, the URAs also use an air to natural gas ratio with a correction for sub/super stoichiometric combustion.

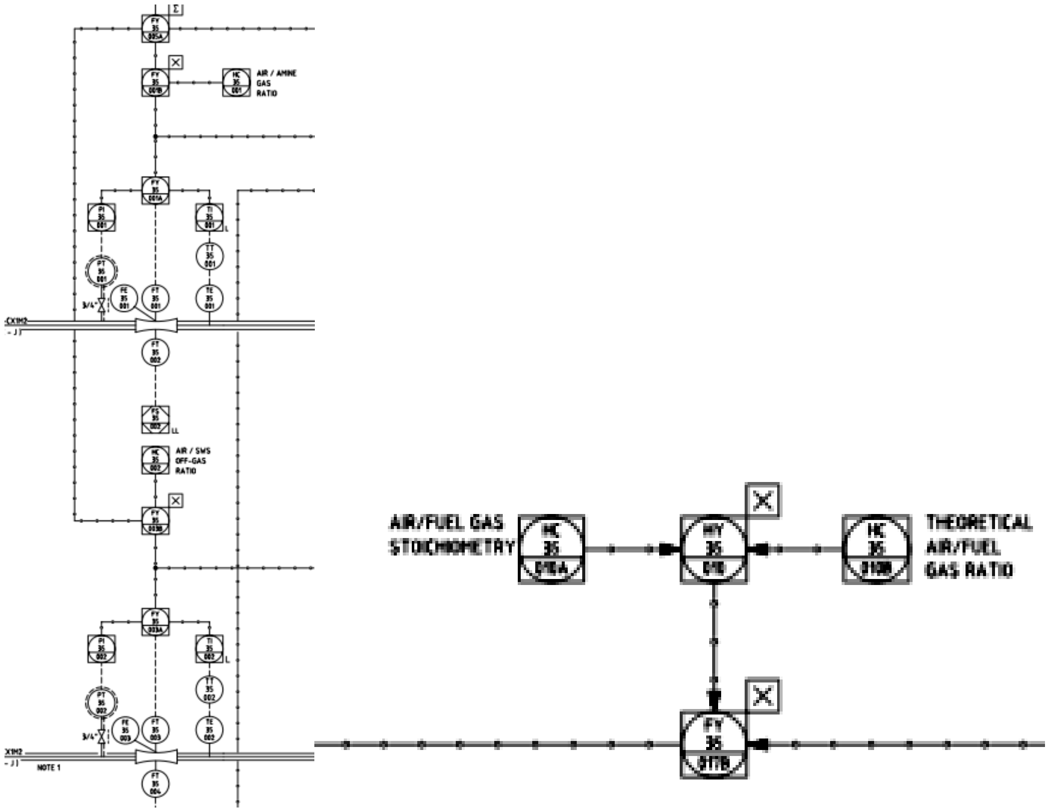

Figure 20. Air to Acid Gas and Air to Natural Gas calculation blocks URA3.

The value of these ratios is essential for the management of the combustion air control during fluctuations in acid gas flow. If the values are set incorrectly, it will result in a potential over or under response from the control system, resulting in a potential upset at the tail gas analyzer. For instance, if the air to amine acid gas ratio value is set too high, it means that too much air is added when the amine acid gas flow increases. As a result, the H_2S concentration at the tail gas analyzer will drop and the emissions will increase temporarily until the tail gas analyzer reduces the air flow again.

Comprimo observed that the board operators will adjust the air to acid gas ratios to bring the output of the tail gas analyzer close to 50% again. In principle this is the correct procedure, however it is important to consider which air to acid gas ratio is changed (Amine gas or SWS gas). If the incorrect ratio is adjusted, it could lead to greater upsets due to acid gas flow changes, which is a very common occurrence at Aconcagua due to the Adverse Conditions Operation. The SWS Acid gas flow is changed substantially twice a day, resulting in substantial emissions upsets during the transition. Comprimo observed that the air to acid gas ratios appeared to be quite removed from the theoretical values, so some concerted effort will be required to find the optimal ratios again.

A procedure was provided to ENAP for modifying the air to acid gas or air to natural gas ratio to ensure minimum impact to emissions during changes in acid gas flow. It is important to only change air to acid gas ratios when the output from the tail gas analyzer has been removed more than 2-3% from 50%.

3.5.4 Analyzers

The Aconcagua refinery currently has Ametek 880 analyzers for the tail gas analysis in URA1 and URA3 and an Ametek 888 analyzer in URA2. There are only minor differences between the two types of analyzers and there is no recommendation to upgrade the analyzers to newer models. There were a lot of discussions between Comprimo and ENAP regarding the reliability of the analyzers due to observed plugging of the sampling system and pressure transducers. As a result of the regular failure, the operators are always concerned that the analyzers are not working correctly and request support from the Instrument technicians to inspect the analyzers.

The issues with the analyzers can be brought back to two main issues:

- Insufficient heating of the sampling system due to insufficient pressure of the LP steam compared to the recommended steam pressure from the vendor Ametek
- Absence of a sulfur condenser in URA3 upstream of the analyzer, resulting in high temperature of the process gas entering the analyzer while saturated with a high sulfur vapour content.

In URA2 and URA3 it is possible to raise the internal LP steam pressure from 3.5 kg/cm^2g to 5.0 kg/cm^2g by changing the setpoints of the LP steam pressure controllers. This will increase the steam temperature from 148°C to 160°C, which should help ensuring that the sampling system will remain clear of solid sulfur. In URA3, where the sulfur vapour content is higher, the pressure transducer setpoint shall be decreased to 0.8 kg/cm^2 to reduce the amount of tail gas flow (and thereby sulfur) entering the sample system.

The operation and maintenance activities with the analyzer technicians were discussed during a meeting at site as well as virtually, and the general observation was that the technicians are experienced and have the right approach to maintain the analyzers. There are a number of times that the operators request maintenance of the analyzers due to process fluctuations when no issues are found with the analyzers.

The following indicators can be used to determine whether an analyzer is not working properly versus process fluctuations:

- The movement of the H_2S and SO_2 shall always be in the opposite direction. If the H_2S reduces, the SO_2 concentration has to go up as well. If this is observed, a process upset is likely the scenario that needs to be considered.
- If there is no movement of the tail gas compositions even during upsets of the unit, it likely means that the sampling system is plugged and an instrument technician shall be brought in to inspect the sampling system
- The temperature profile in the URA2 and URA3 SUPERCLAUS® reactors can be used as an indicator of whether the tail gas H_2S concentration is in line with the temperature rise in the catalyst. As a rule of thumb, the temperature in the reactor should rise about 60°C per % H_2S in the tail gas analyzer.
    - Due to the problems in URA2 with sulfur carryover at the moment, this is harder to investigate, however after the outlet channel of the third condenser is cleared, the catalyst should start behaving as expected again.
- Observation of the pressure transducer on the analyzer sampling system should indicate whether there is a problem with plugging as well.
- Always evaluate whether the traps on the sampling system steam supply are working properly by checking the temperature of the jackets with a piece of sulfur. If the sulfur melts, the system is flowing with steam.

3.6 KEY PERFORMANCE INDICATORS

Key Performance Indicators (KPI) employed by ENAP to monitor the operation of the Sulfur Treating Units were reviewed by Comprimo and typical examples of the recommended KPIs for SRUs, SWSs and ARUs are provided in this paper in Table 1.

Table 1. Recommended Key Performance Indicators (KPI)

Operational KPI	Reliability KPI	Good to see	Plant	Parameter	Min. Limit	Max. Limit	Target	Notes
		X	URA 2	Amine Load [kg/h]	400	1400	1100	Modify minimum trip setpoint
		X	URA 2	SWS Load [kg/h]	-	-	-	Modify minimum trip setpoint
		X	URA 2	Efficiency [%]	98	99.5	99	
		X	URA 2	Production [ton S/d]	-	-	-	
X			URA 2	AAG/SWAG Ratio[ad]	1	1.3-	1	NH_3 not more than 25 vol% in mixed acid gas
X			URA 2	Relative Load	0.26	0.9	0.3	
	X		URA 2	Combustor Temperature [°C]	1250	1500	1275	
X			URA 2	Combustor Pressure [kg/cm2]	0	0.7	0.6	
	X		URA 2	Normalized Pressure [ad]	0	60	40	
X			URA 2	Trim Air Control [%]	45	55	50	Tail gas controller output
X			URA 2	Air/AAG Ratio	1	2	1.5	
X			URA 2	Air/SWAG Ratio	1	2	2.1	
		X	URA 2	SO_2 Emissions [ton SO_2/d]	0	0.624	0.6	
X			URA 2	SO_2 Stack Concentration [ppm]	0	2000	1600	
X			URA 2	Bottom Temperature D-1641 [°C]	290	310	300	
X			URA 2	Bottom Temperature D-1642 [°C]	200	220	210	
X			URA 2	Bottom Temperature D-1643 [°C]	245	270	260	
X			URA 2	Concentration SC H_2S [%]	0.6	0.8	0.65	
X			URA 2	Concentration SC SO_2 [%]	0	0.08	0.06	

Operational KPI	Reliability KPI	Good to see	Plant	Parameter	Min. Limit	Max. Limit	Target	Notes
X			URA 2	Condenser Temperature C-1645 [°C]	120	140	130	
		X	URA 2	pH C-1641	7.5	10		
	X		URA 2	Condensate Cond. C-1641 [mS/cm]			5000	
			URA 2	Vapor Cond. C-1641 [mS/cm]				Steam quality not checked
		X	URA 2	pH C-1650	7.5	10		
	X		URA 2	Condensate Cond. C-1650 [mS/cm]			5000	
			URA 2	Vapor Cond. C-1650 [mS/cm]				Steam quality not checked
		X	URA 2	pH C-1641/42/43 (triplet)	7.5	10		
		X	URA 2	Triplet Condensate Cond. [mS/cm]			7000	
	X		URA 2	Dissolved oxygen C-1650 [mg/l]			0.007	
	X		URA 2	Dissolved Oxygen C-1641/42/43 (triplet) [mg/l]			0.04	
		X	SWS 1	Plant Load [m^3/h]	18.75	45.83	30	
			SWS1	Steam/Sour Water Feed Ratio [ad]	150	250	170	
	X		SWS 1	Overhead Temperature E-1501 [°C]	80	90	90	
			SWS 1	Cold Pumparound Temperature [°C]	60	80	75	
		X	SWS 1	Overhead Pressure E-1501 [kg/cm^2g]	0.85	-	1	
		X	SWS 1	Stripped Water pH	5.5	9	7	
X			SWS 1	Sulfur in Stripped Water [ppm]	0	10	5	
X			SWS 1	NH_3 in Stripped Water [ppm]	0	40	8	
		X	ARU	Plant Load [m^3/d]	3000	3500	3200	
X			ARU	Differential Pressure E-3201 [kg/cm^2]	0.2	0.3	0.28	
X			ARU	Overhead Temperature E-3201 [°C]	105	115	110	
X			ARU	Reflux Return to Tower (FC-32005) [°C]	60	120	60	
X			ARU	H_2S Lean Amine loading [mol/mol]	0	0.01	0.01	
	X		ARU	H_2S Rich Amine loading [mol/mol]	0	0.45	0.25	

Operational KPI	Reliability KPI	Good to see	Plant	Parameter	Min. Limit	Max. Limit	Target	Notes
X			ARU	DEA Concentration [wt%]	250	300	260	
	X		ARU	Ammonia Bisulphide Salts Content (%)	3	5.25	4	Reflux water
		X	ARU	pH Reflux Water	7	9	8	
	X		ARU	Heat Stable Salts [wt%]	0	2.5	2.00	
X			ARU	Overhead Pressure E-3201 [kg/cm^2g]	0.85	1.2	1.05	
	X		ARU	Bottom Temperature E-3201 [°C]				
X			ARU	Reflux Temperature [°C]	35	50	40	
		X	ARU	Matrix #150 [kg/cm^2g]	10	11	10.5	ARU reboiler steam

4.0 OPERATOR EXPERIENCE REVIEW

4.1 QUESTIONNAIRE

Comprimo evaluated the level of expertise within the Aconcagua refinery organization by preparing an anonymous questionnaire that covered the following topics:

- Role in organization and experience
- Experience in sour water stripping
- Experience in amine regeneration
- Experience in sulfur recovery
- Knowledge of safety systems

The questionnaire was sent out to a total of 45 people in the organization and 25 responses were received distributed as follows across the organization:

- Engineering: 2
- Board Operators: 7
- Field Operators: 12
- Supervision: 4

4.2 RESULTS

The answers were evaluated and the percentage of correct responses for each question was determined per group within the organization. Fully correct answers were considered as 100% correct and partially correct answers were provided with partial scores. If there were multiple correct answers in a question, the scores were reduced when part of the answers were missing. The results were tabulated, and colour coded to get an indication of the general overall knowledge of the different areas of the sulfur treatment units.

The following observations can be made about the level of knowledge of the units that are installed at the Aconcagua refinery:

- Across the board the field operators have the lowest knowledge of the units that they are operating.
    - This is not unexpected, as the field operators do not need to have an intimate knowledge of the actual operation of the facilities.
    - With the organizational plan currently in place to have the field operators eventually grow and move into a board operational role, it is important for them to understand the full operation of the units

- The scores of the engineers were on the low side, especially on the safety side.
    - The engineers should be the most familiar with the design and operation of the sulfur treatment units and be able to train the board and field operators on a continuous basis.
    - Typical practice in the industry is to rotate process engineers in the sulfur treatment units rapidly to give them more exposure to the other refinery units
        - This means that there is limited experience time for the engineers on the Sulfur Treatment Units, which results in more dependence on the experience of operators and supervisors.
    - ENAP currently does not have an internal SME (Subject Matter Expert) in the sulfur treatment units, which means that experience tends to not be retained in the units
        - Common practice in larger oil companies is to have a central Subject Matter Expert who oversees the training of new engineers, manages new projects in the sulfur treatment unit, provides assistance with start-ups and shutdowns and attends conferences to improve the overall learnings of the facility
- The board operators scored about 50% on average across the board with lower scores in the Sour Water Strippers
    - Due to the long-term issues with the operation of the SWS, it appears that some temporary resolutions to operating problems have become permanently learned behaviours.
    - After maintenance of the units, it is recommended to retrain the board operators on what the correct operating parameters of the units should be.
- The people in supervisory roles all tended to score in the 50% range as well. It is of note that one person was not able (or chose not) to answer most of the questions, which lowered the results substantially.
    - Depending on the level of supervision required, this can lead to potential operational issues. Comprimo observed that the Board Operators and Engineers had limited autonomy to make decisions about the operation and there appeared to be strong culture of requiring approval from the Supervisors to make any changes to the operation, even if it was recommended by the licensor/subject matter experts.

5.0 TURNAROUND URA2

URA2 went through a turnaround between April and July of 2023. Comprimo was engaged to support the inspection of the equipment after shutdown of the units and provide recommendations. The main observations of the inspection are presented in this section.

5.1.1 Main Burner B-1641

- The main burner was removed from the thermal reactor and the natural gas gun was removed from the burner
- There is indication of substantial back firing on the burner nose cone, resulting in damage to the nose cone.

Figure 21 - Natural Gas Gun and Nose Cone Damage

- There is also evidence of back burning on the opening into the mixing chamber as well as deformation of the nose cone of the air chamber, which can lead to bypass of air around the swirl vanes of the burner

Figure 22 - Main Burner and nose cone into the Mixing Chamber

5.1.2 First, Second and Third Condenser (Triplet) C-1642/C-1643/C-1644

- The front head and the rear head of the triplet condenser were removed for access to the tubesheets
- The front tubesheet was inspected and it was noted that there were a number of tubes plugged in all three condensers
- The back tubesheet was also inspected and there was evidence of the plugs wearing
  - Per discussion with Operations and Maintenance, the tubes will be replaced during this turnaround.

- The outlet channels of all three condensers were inspected and it was found that especially the second and third condenser showed a large build-up of foreign material that does not appear to be sulfur.

Figure 23 - Foreign Material in the Outlet Channel of the Second Condenser

- In addition, the foreign material was partially to fully blocking the sulfur rundown nozzle in the outlet channel for the second and third condenser

Figure 24 – Second and Third Condenser Outlet Channels

Figure 25 -Second and First Condenser Outlet Channels

This is expected to be the main cause of the poor performance of URA2. As the sulfur cannot flow properly out of the second and third condenser, sulfur is carrying over to the second reactor as well as the third reactor. During the technical review in 2022, there was evidence that liquid sulfur was draining down the catalyst. The temperature profile in the third reactor showed evidence of sulfur vaporization in the catalyst.

5.1.3 Second Reheater C-1648 Tube Bundle

The second reheater had experienced a leak in the tubes in January of 2023 and upon inspection, it was observed that three tubes had been plugged. There also was evidence again of debris and soot in the shell and on the tubes of the reheater.

Figure 26 -Second Reheater Inspection

5.1.4 Third Reheater C-1649 Tube Bundle

- Substantial fouling was observed on the shell side of the reheater as well as fouling of the tubes
- There was evidence of some elemental sulfur in the fouling material, however there was also evidence of black material that appeared to be potentially soot as well white material which may be catalyst or refractory

Figure 27 - Fouling material on tubes third reheater

- The inlet nozzle appeared to be full of a fine black material after the pulling of the tubes. This could be either iron sulfide or even soot based on the findings in the reactors. The amount of fouling material is substantially higher than typically expected in a third reheater.

Figure 28 - Fouling on third reheater tubes

Figure 29 - Fouling on third reheater tubes/fouling in inlet nozzle third reheater

5.1.5 First Reactor D-1641

- There was clear evidence of substantial amounts of soot on the catalyst in the first reactor. Soot is indication of substoichiometric combustion of fuel gas/natural gas in the main burner. It could also be indication of inefficient combustion during continuous co-firing of the burner. There is also indication from operations that the burner had operated in severe turndown for extended periods, which appears evident through the burner damage.

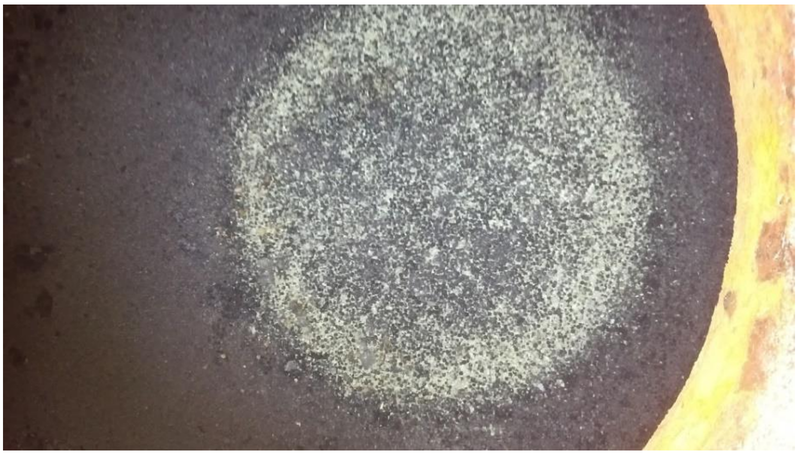

Figure 30 - Top view catalyst first reactor

5.1.6 Second Reactor D-1642

- There is evidence of soot deposits on the second reactor as well, which is unusual as there is no inline fired reheater upstream of the reactor. This is evidence that the first reactor is completely saturated with soot, with the soot breaking through to the second reactor.
- In addition, it appears that part of the catalyst has pulverized into a fine powder, indicating that liquid water had been present in the reactor. The source of water into the catalyst needs to be determined. This could be a leaking second reheater or that the snuffing steam connection available on the reactor (see Figure 32) was left open.
- Comprimo provided the following recommendations:
    - Remove and replace the catalyst. Determine the depth of the soot in the catalyst bed.
    - Inspect the grid underneath the catalyst. Operations indicated that during one of the last catalyst replacements, mesh was installed over the grid.
    - Never use the snuffing steam connection available on the first and second reactor and keep the connection blinded. The procedure in case of fire in the reactor should be to lower the amount of air to operate substoichiometric in air.

Figure 31 - Top view catalyst second reactor

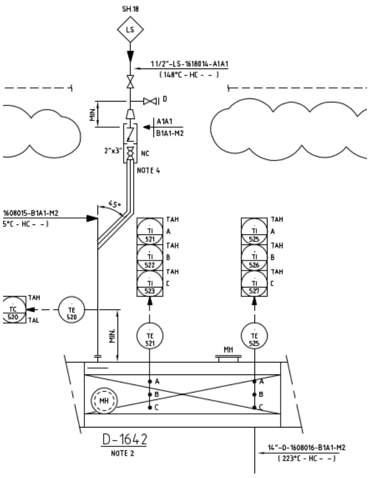

Figure 32 - Steam Connection to Second Reactor

5.1.7 Third Reactor (EUROCLAUS Selective Oxidation Reactor) D-1643

- There is evidence of sulfur on top of the catalyst in the third reactor as well as some soot

- Comprimo provided the following recommendations:

  - Remove and replace the catalyst. Determine the depth of the soot in the catalyst bed. Remove the sample baskets from the reactor for catalyst sampling
  - Observe the catalyst damage on both sides of the reactor. During operation there was evidence that there was preferential flow of potentially sulfur (as evident from the plugging of the sulfur outlet nozzle in the third condenser) to one side of the Third Reactor

Figure 33 - Top View Catalyst Third Reactor

6.0 START-UP/OPERATION AFTER MAINTENANCE

After almost two months of an “interrupted” turnaround, the URA2 started its operation in mid July 2023. In a joint effort between ENAP and Comprimo, on July 20th, 2023, the unit began the conditioning process for Hydrogenation and Selective Oxidation catalysts.

One of the main issues found during the start up of URA2 was that the maintenance department had failed to recognize the severity of the reduction of remaining life of the reheaters even though Eddy Current testing had been performed on the tubes.

During start-up of the unit, water was found to be pouring out of the sulfur rundown of the second condenser, indicating that there was either a condenser leak or a reheater leak. With the BFW valve closed, the water level did not change indicating a leak in the reheater. Five new holes were found in the reheater and the leaking tubes were plugged, however after hydrotesting an additional 5 tubes started leaking. At that point the plant decided to retube the exchanger, causing an additional one week delay in start-up, and order stainless tubes for the next turnaround for all (P)reheaters.

Figure 34 – Tube Failure: Second Reheater after removal of the tube bundle

As the refinery was in the middle of an FCC turnaround as well, there was low acid gas availability to do a proper conditioning activity. At that time, the available feed was only enough to reach a relative load (actual air demand to design air demand ratio) of 30%. This value was far from the recommended 50% value according to Comprimo standards. Therefore, to assure a correct conditioning and after a combined review of both parts, the decision of feeding amine and sour water acid gases was taken (natural gas was also fed to the unit to increase the relative load of the unit).

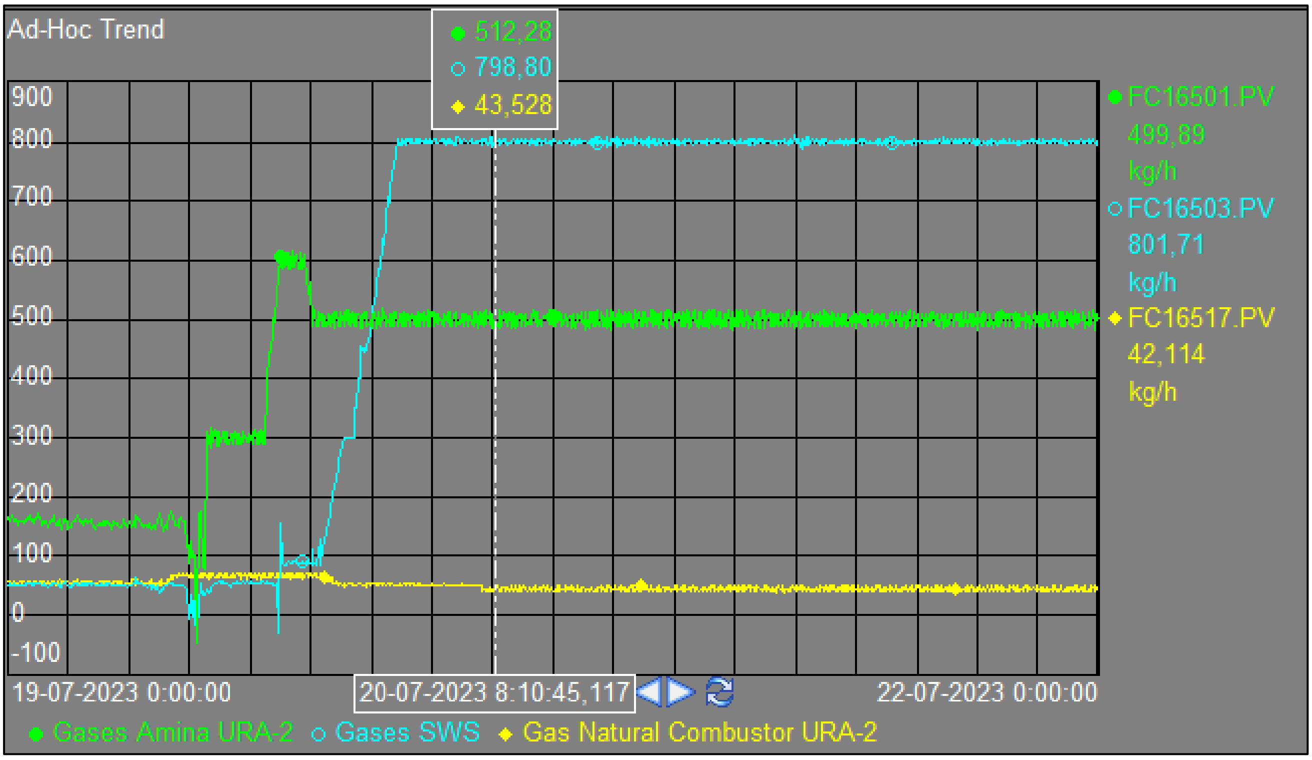

Figure 35 – Feeds to URA2 during conditioning (green: AAG, light blue: SWAG, yellow: natural gas)

The activity lasted around eight days. Figure 36 and Figure 37 exhibit the behavior of the Selective Oxidation reactor during the whole process. Following Comprimo's recommendation, especially those that focused on to avoiding 2020 mistakes, ENAP was able to perform a proper conditioning without neither upsets in the H_2S inlet concentration nor temperatures runaways.

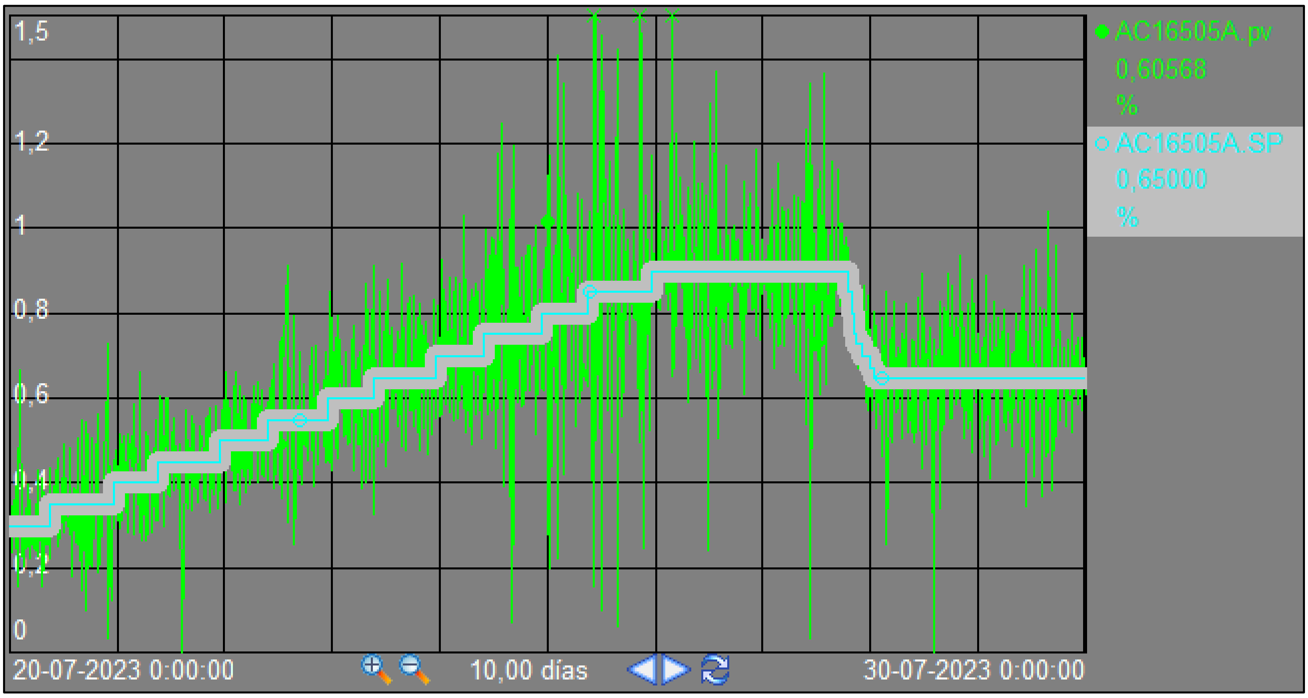

Figure 36 – Trends of tail gas analyzer values (AC16505A.PV) and setpoint (AC16505A.SP)

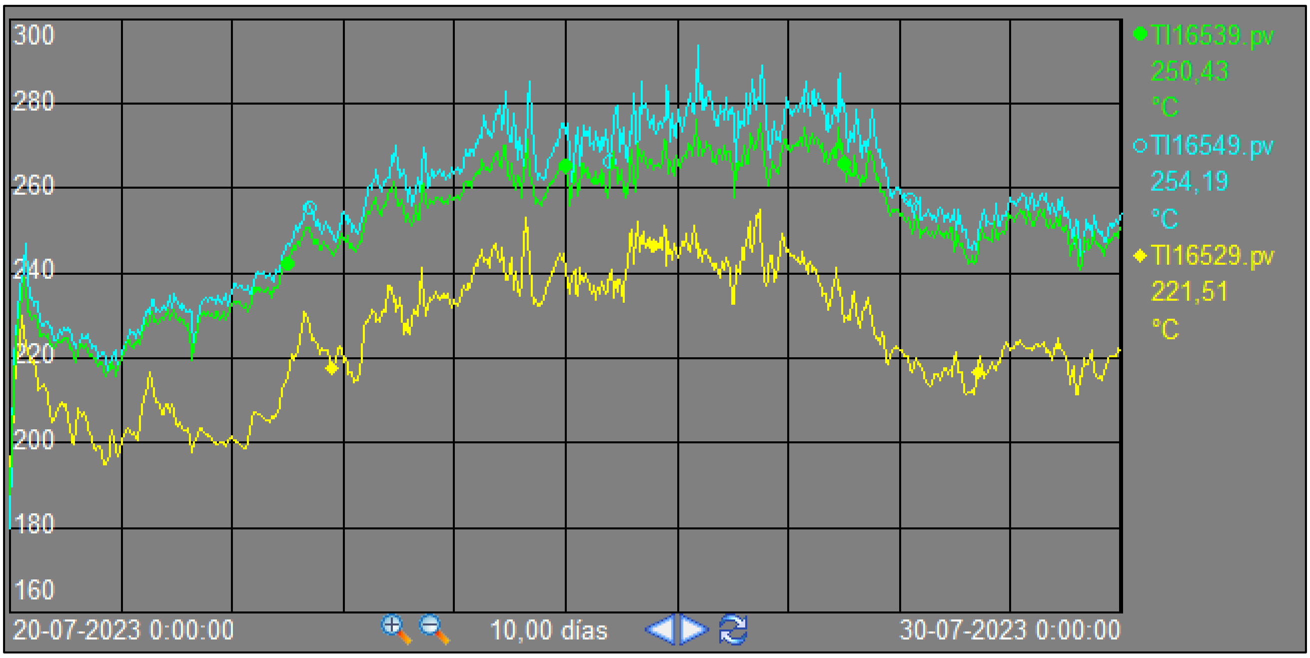

Figure 37 – Selective Oxidation reactor temperatures at different depths (yellow: top, green: middle, light blue: bottom)

Additionally, SO_2 stack emissions were under control during all the process and no visible plume was seen (Figure 38 shows the SO_2 emissions trend for those days). Finally, from the eighth day onwards, the emissions decreased to the values expected according to the quality of the feed processed in the unit.

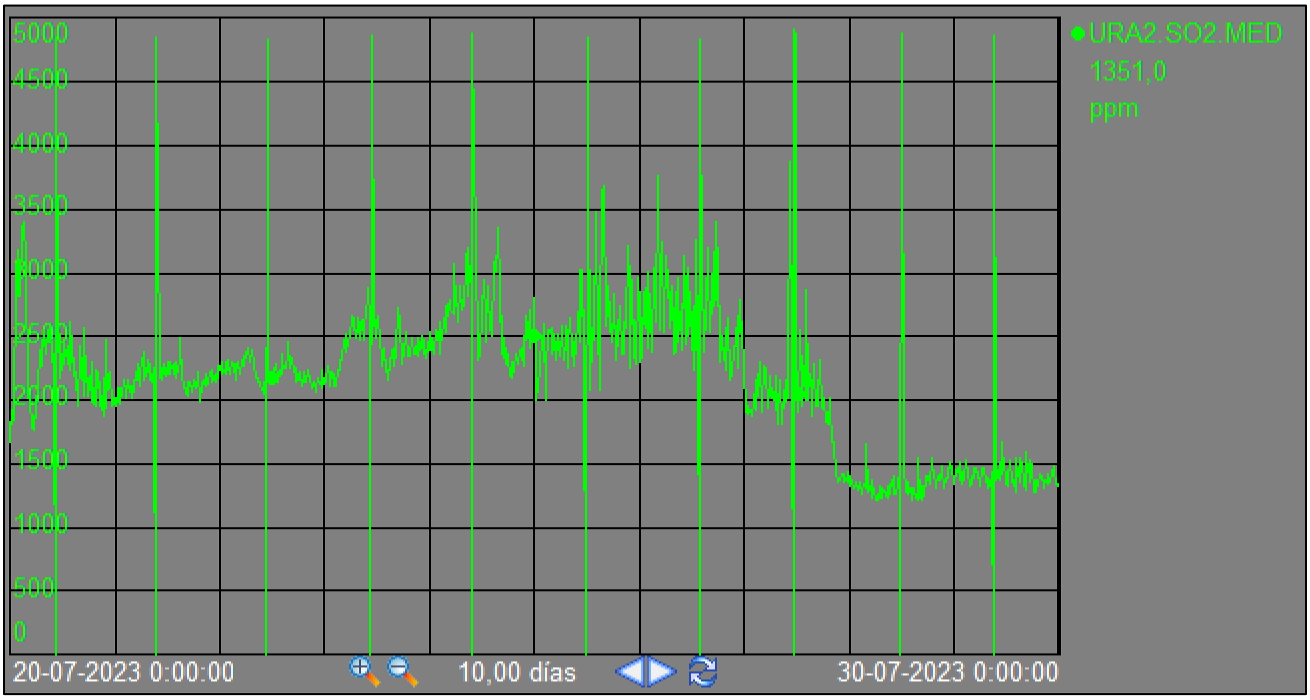

Figure 38 – Stack SO_2 analyzer (spikes and "zeros" are CEMS QA/QC tests)

7.0 CONCLUSIONS

Comprimo performed a thorough technical review of the sulfur complex at the ENAP Aconcagua refinery to determine what design, operations and maintenance practices could be limiting their ability to meet processing run lengths as well as environmental targets on a continuous basis.

The review has provided ENAP with a better understanding of design limitations of their existing units, as well as any limitations in their ability to operate their units to meet the required emissions targets by the government. Comprimo provided clear KPIs for all of the units that will allow the operators to maintain the units within the recommended operating limitations, thereby maintaining better performance and longer life of the units.

One of the main conclusions of the review was a lack of understanding of the importance of proper heating of the piping and equipment in a sulfur plant. It is essential to have the design of the heating system of a sulfur recovery done by an experienced company well-versed in the calculation of heat losses in a system where sulfur freezes below 120 °C (248°F).

The recommendations for URA2 were implemented in a recent turnaround and the plant has been maintaining emissions in this unit since the start-up, with the release of SO_2 from this unit reduced by half. The support of Comprimo allowed ENAP to perform a well-executed conditioning of the EUROCLAUS Selective Oxidation Catalyst under circumstances that the plant otherwise would have been uncomfortable with. This will set ENAP up for successful start-ups in the future. Additional learnings from the technical review are planned to be implemented in the SWS and amine regeneration unit, however these changes will be made in future turnarounds. Comprimo has provided recommendations for these units as well as some recommendation for the design of the new SWS and WSA units to be installed in the near future.