ENAP Integrates Gas Cleaning Systems for Emissions Controls ON All FCCUs

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Synopsis

A fluid catalyst cracking unit (FCCU) is often one of the key process units in many refineries. It can also be a major source of atmospheric emissions. As refiners all over the world look to lower emissions, some are taking actions to decrease FCCU flue gas emissions. As part of a recent FCCU revamp, Enap Refinerias S.A. (ENAP) commissioned a wet scrubber to control FCCU flue gas emissions at the Bio Bio Refinery in Hualpen, Chile. The revamped FCCU and new scrubber were successfully commissioned in August 2019. This was ENAP's first experience using a wet scrubber with an FCCU. It is also the first scrubber operating on an FCCU in South America. ENAP's strategic plan also includes the installation of a second wet scrubber on the FCCU at the Aconcagua Refinery in Concon, Chile, which is currently in the execution phase. This paper discusses how these major emissions control projects evolved, how and why technologies we selected, and emissions control results.

Introduction

To better understand the reality of what drives environmental projects today, we must look back at recent history. We would like to highlight two factors we feel are fundamental in explaining large environmental investments today by the oil refining industry, as well as in the industry in general.

- Environmental Awareness
- Population Growth

Both factors contribute to the current environmental scenario and place stricter rules for the industry.

Environmental Awareness - Over the last 50 years there have been great advances in environmental issues that permeate our society, communities and industries. There is demand for greater care for the environment that has driven regulations, agreement and compliance with these. While we may have different opinions as to when our environmental awareness and actions started, we feel that much started with the Stockholm Conference in 1972. Following the conference Latin America environmental organizations (and associated government ministries), as well as green political parties were born. A second important event is the creation of the World Environment Commission in 1984. This committee initiated the concept of sustainable development with the Brundtland report "Our Common Future" in 1987. A third relevant event is the Rio Summit of 1992 that provides the concept that it is possible to incorporate environmental protection as a requirement in economic treaties. The fourth event to highlight is the Paris Agreement in 2016. Apart from the massive number of countries that have participated, two points can be highlighted; It recognizes a relationship between human rights and climate change, and generates an agreement to avoid a 2°C increase in the planet's temperature. Finally, there is the Escazú agreement in 2018. This validates access to information, public participation and justice in environmental issues for Latin America. All this progress in environmental awareness has opened spaces for communities to claim and demand environmental protections for future projects in all areas of industry.

Demographic Growth and Neighboring Communities - The ENAP Aconcagua refinery and ENAP Bio Bio refinery were built during the 1950s and 1960s. At that time, the areas around the refineries were far from the cities and not populated. Today, more than 60 years later, the landscape around each refinery has changed markedly. We understand the construction of a refinery favors the formation of an industrial hub necessary to support operations and maintenance, as well as to take advantage of the refinery's products. All this industrial development mobilizes workers with their families to be closer to work, promoting the development of commerce, schools, public offices for procedures, etc. Although at the beginning of operations there were no communities abutting the refineries, today communities are just at the other side of each refinery's fence. Considering this, it is understandable that events at the refinery, such as poor operation, and new projects that change the current status, will immediately impact the community around the refinery. This situation is not particular of only the refineries at Chile, they can be seen in Argentina and other Latin American countries whose refineries have in operation for more than 20 years.

These factors put pressures on authorities to take care of the environment of neighboring communities and implement increasing more stringent environmental emissions requirements.

Figure 1 - Area of Bio Bio Refinery

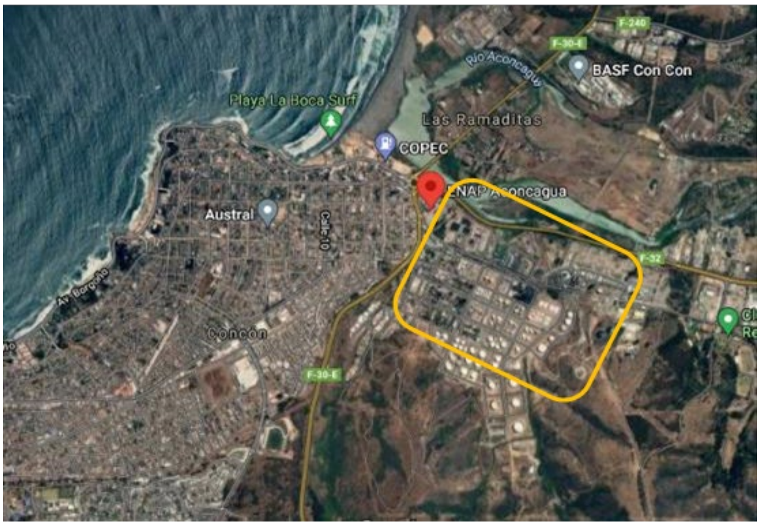

Figure 2 - Area of Aconcagua Refinery

New Environmental Regulations - In 2018 the government in Chile, through the environmental authority, decreed new environmental regulations requiring reduction of sulfur dioxide (SO_2), nitrous oxides (NO_x) and particulate matter (PM) emissions. For companies in each sector, the authority prepared a baseline for each emissions parameter and decreed new values to be met within a certain period.

The table in figure 3 shows the annual emissions requirements for the Aconcagua refinery. This requires an emissions reduction of 1,269 tons per year. A significant investment is required to meet this.

En ton/año	Emisiones Mar/2019	Emisiones Mar/2022	Reducción
SO_2	1.492	1.145	347 (23%)
MP	918	230	688 (75%)
NO_x	1.169	935	234 (20%)

Figure 3 - Annual Emission Requirements for Aconcagua Refinery

At the Bio Bio refinery, ENAP had some years earlier taken the path towards reducing emissions. This involved promoting a major investment project that include reducing emissions. This is how, the refinery began evaluating ways to reduce emissions that comply with the requirements of the authority and that support sustainable operation over time. In undertaking a review at the refinery, it was observed that the main source of particulate matter and sulfur dioxide emissions is the fluid catalytic cracking unit (FCCU). This finding was important directed evaluation towards what technologies could best be used to reduce emissions from the FCCU.

Technologies to Reduce FCCU Emissions

At the Bio Bio refinery ENAP operates an FCCU licensed by UOP and asked UOP to help explore different technologies that could meet the requirements. The technologies evaluated were:

- Third Stage Separation System (TSS)
- Electrostatic Precipitators
- Wet Gas Scrubber (WGS)

Third Stage Separation System (TSS) – A TSS adds an additional stage of cyclonic separation downstream of the regenerator cyclone in the high pressure flue gas section to capture and remove the particulate matter. This approach requires the use of SO_x control additives within the FCCU to reduce sulfur dioxide emissions. Particulate removal is about 75% to 78%. This has a smaller footprint requirement and slightly lower investment cost compared to using a WGS.

Electrostatic Precipitator (ESP) - An ESP is designed to capture and remove particulate matter with electrostatic collection in the flue gas downstream of the regenerator in the low pressure flue gas section. Like with TSS, this approach requires the use of SO_x control additives within the FCCU to reduce sulfur dioxide emissions. Particulate removal is about 95%, about the same as with the WGS. This requires a footprint much larger than the TSS. The investment cost is lowest of the three alternatives.

Wet Gas Scrubber (WGS) - The WGS is designed to capture and remove both particulate matter and sulfur dioxide downstream of the regenerators in the low pressure flue gas section. It can also be considered for control of NO_x emissions. Particulate and sulfur dioxide removal exceeds 95%. Unlike with the TSS and ESP, use of SO_x control additives within the FCCU are not required to reduce sulfur dioxide emissions. This requires the largest footprint of the three alternatives and has the highest investment cost.

Considering the above, ENAP decided to pursue the use of the WGS alternative to reduce atmospheric emissions from the FCCU at the refinery. Following this, ENAP hired an independent company to evaluate available WGS technologies. The BELCO® scrubbing technology was selected and considered the following items.

- Operational Flexibility - It presented the best abatement yields independent of the operational variations presented by the unit.

- Water Consumption - It has a lower water consumption compared to the competition.

- High Reliability and Low Risk - It presents a design that allows it to be adapted to FCC arrests and does not have major risks to the operation.

- Market Share - It is the technology with the greatest presence in the refining industry.

Understanding FCCU Emissions

For many refiners the combustion flue gas from the FCCU regenerators is the single largest point source of atmospheric emissions in the refinery. The flue gas is primarily a mix of nitrogen (N2), carbon dioxide (CO_2), water (H_2O) and oxygen (O_2), but also contains some carbon monoxide (CO), particulate, sulfur oxides (SO_x as SO_2 and SO_3), and nitrogen oxides (NO_x as NO and NO_2). CO is controlled mostly within the regenerator using process control, process optimization and/or combustion promotion additives. These and CO combustion boilers or CO incinerators are typically used for partial burn regenerators. ENAP will control CO emissions to required levels within the regenerator.

Particulate matter (PM) emissions result as catalyst fines escape the regenerator cyclones that process the flue gas within the regenerator. The cyclones remove the larger size regenerated catalyst from the flue gas and return the catalyst back to the FCCU process. Smaller size catalyst fines are too small to be removed by the cyclones and remain entrained in the flue gas. A large portion of the entrained catalyst fines range from 20 micron to below 1 micron in size. Some larger size particulate may be also present.

In the cracking process a portion of feed sulfur becomes bound with the coke that forms on the catalyst. As the coke is combusted in the regenerator, SO_x forms as the sulfur is combusted (oxidized) and is part of the flue gas. A large portion forms SO_2 and a very small portion forms SO_3. As with SO_x, NO_x also forms in the regenerator and is part of the flue gas. NO_x forms as portions of feed nitrogen and portions of combustion air nitrogen are oxidized. A large portion forms NO and a very small portion form NO_2. ENAP will control NO_x emissions to required levels within the regenerator.

Controlling FCCU Emissions with BELCO® Scrubbing

BELCO® scrubbing has been used extensively to control flue gas emissions from FCCUs worldwide. Over 150 units have been licensed for use on FCCUs. This includes three units in South America, with one unit operating on the FCCU at the ENAP Bio Bio refinery, one unit being completed on the new FCCUs at the Petroperú Talara refinery, and the one unit being designed/constructed for the existing FCCU at the ENAP Aconcagua Refinery.

The BELCO® scrubbing system for ENAP Bio Bio refinery is configured to treat the flue gas and control both particulate and SO_x emissions to required levels. It is being installed downstream of the regenerator and wasted heat recovery. It consists of a separate scrubber section for flue gas cleaning (emissions control) and a separate purge treatment unit (PTU) section for handling/processing liquid discharged from the scrubber sections. The installed scrubber section is shown later in figure 6. The installed PTU is shown later in figure 8

A basic process flow diagram follows in figure 4 and shows the major process streams and sections.

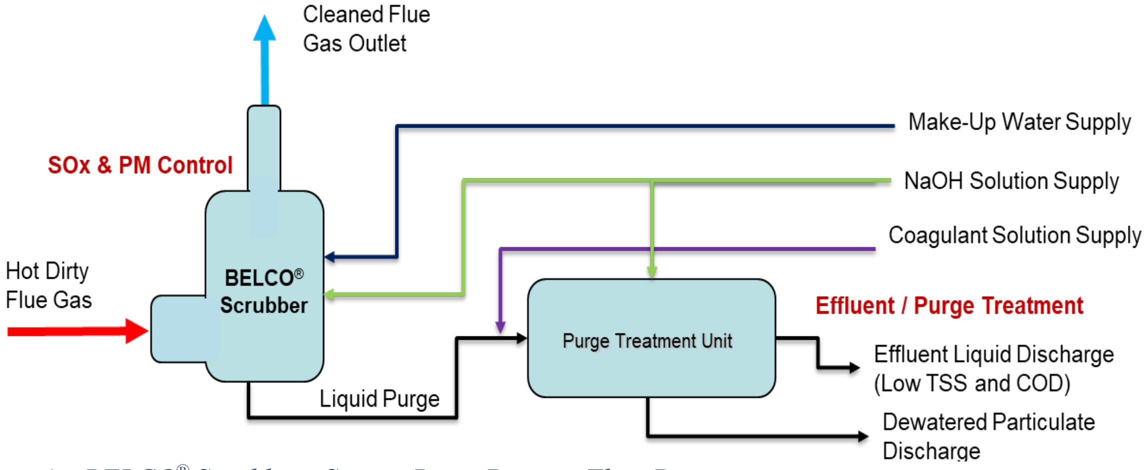

Figure 4 – BELCO® Scrubbing System Basic Process Flow Diagram

Hot dirty flue gas from the upstream FCCU regenerator and flue gas cooler enters the scrubber section and leave the stack as cool clean flue gas. Water evaporates in scrubber section and make-up water is added to support the process. NaOH solution is added to the scrubber section to support the absorption and neutralization of SO_2 and SO_3 removed from the flue gas, and to maintain a neutral pH. A liquid purge is discharge from the scrubber section to the PTU section. This stream contain the catalyst fines, SO_2 and SO_3 removed from the flue gas.

The SO_2 and SO_3 removed from the flue gas become dissolved sodium sulfate (Na_2SO_4) and sodium sulfites ($NaHSO_3$ and Na_2SO_3) is the liquid purge. In the PTU section the sulfite are oxidized to sodium sulfate to minimize the chemical oxygen (COD) demand of the final effluent liquid. NaOH solution is added to the PTU section to support oxidation and to maintain a neutral pH.

Catalyst fine removed from the flue gas become suspended solids in the liquid purge. In the PTU section, catalyst fine are removed from the liquid purge to minimize the total suspended solids (TSS) in the final effluent liquid. The catalyst fines removed from the liquid purge are further dewatered to support disposal. A coagulant solution is added to the PTU section to support the process.

A staged low energy wet scrubbing approach is used in the BELCO® scrubber and is shown in figure 5.

Stage A - Quench/Saturation - Hot dirty flue gas enters the horizontal inlet of the upflow scrubber tower. The flue gas is rapidly quenched to saturation as is passes through high-density water curtains produced by specialized spray nozzle(s). Some water evaporates as the flue gas temperature rapidly decreases and the water content rapidly increases. At the same time, a portion of the particulate (catalyst fines), SO_2 and SO_3 are removed by condensation, absorption and impaction with the water curtains.

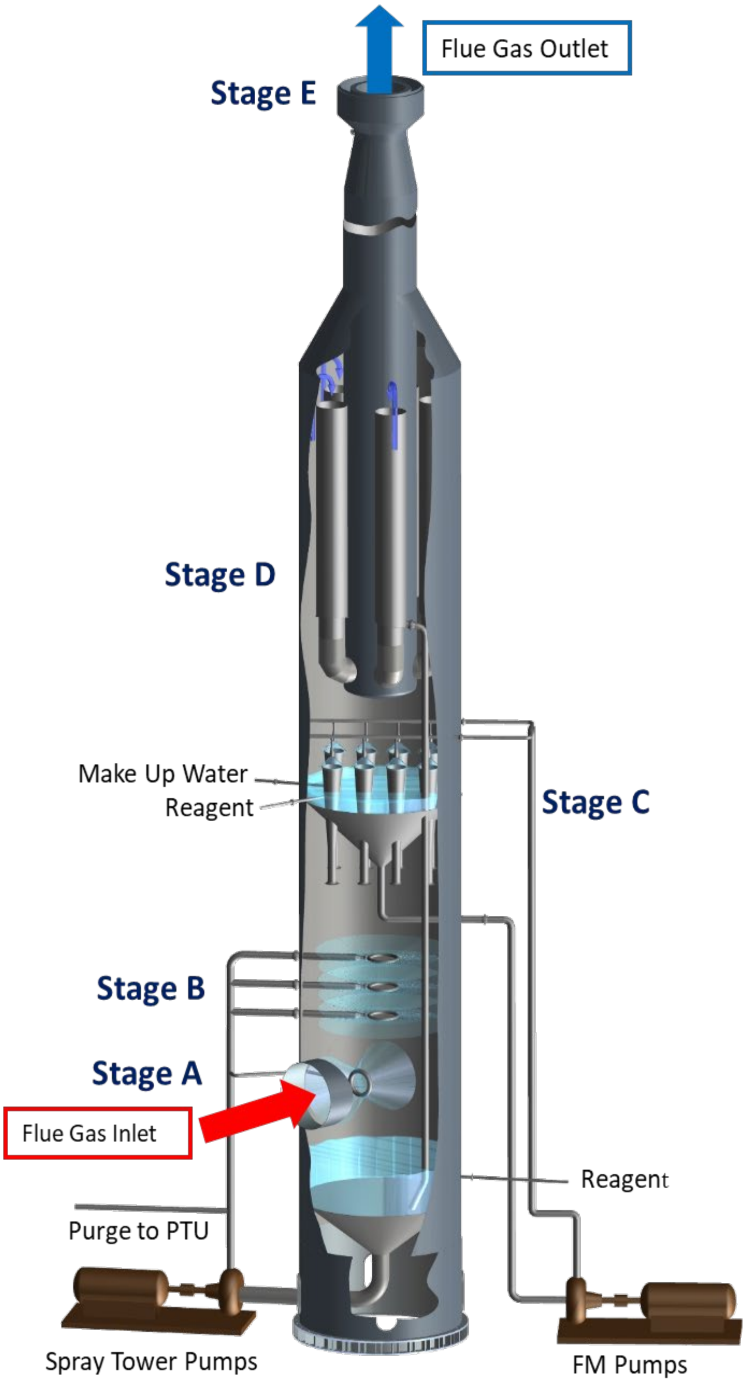

Figure 5 -BELCO® Scrubber Tower

Stage B - Absorption / Particulate Removal – Following the horizontal quench, the flue gas flows up through the upflow scrubber tower. The flue gas is contacted by additional high-density water curtains produced by the same type of specialized spray nozzle(s) used in quenching. Multiple levels of water curtains remove more particulate (catalyst fines), SO_2 and SO_3 are removed from the flue gas. The bulk of the larger particulate (≥ 3 micron) and portion the condensed SO_3 mist are removed by impaction with the water curtains. The bulk of the SO_2 is absorbed through contact with the water curtains.

Water sprayed in the horizontal inlet and the upflow section drains to integral recycle tank at the bottom for the tower. A set up pumps recirculates the water to the process and allow for a small liquid purge to the PTU section. NaOH solution is added the recycle tank to buffer the liquid to a neutral pH.

Stage C - Fine Particulate Removal - As the flue gas flows further up in the tower it is distributed to a set of parallel filtering module tubes. The lower section of each tube has a small dimeter that forces the flue gas to rapidly accelerate (compress). Above the small diameter, the tube diameter gradual increases. This increasing diameter allows the flue gas to gradually decelerate (expand). Compressing then expanding the saturated flue gas drives water to condense from the flue gas. Water condensed on the fine particulate and condensed SO_3 mist in the flue gas. These act as condensation nuclei. Turbulence within each tube allows the water encapsulated fine particulate and condensed SO_3 mist to collide and agglomerate. These increase the size and mass of the entrained fine particulate and SO_3 mist. As the flue gas exists each tube, the gas flows through a high-density water curtain produced by different type of specialized spray nozzle. Each high-density water curtain removes (filters) the now enlarged agglomerated fine particulate and SO_3 mist from the flue gas. Some SO_2 is also removed by absorption as the gas pass through the high-density water curtain.

The water curtain from each spray nozzle sprays past the outlet of each tube and is captured within a conical recycle tank that surrounds the outside of the filtering module tubes. The tank is integral the scrubber tower. A set of pumps recirculates the water to the process. NaOH solution is added the recycle tank to buffer the liquid to a neutral pH.

Make-up water is added to the recycle tank based on water evaporation and water purged to the PTU in the lower portion of the scrubber. Water overflows from this upper recycle tank to the lower recycle tank and carries the captured fine particulate, SO_3 and SO_2 to the lower portion of the scrubber.

Stage D - Droplet Separation - With the use of water sprays in lower sections of the scrubber there will be some entrained (free) water droplet in the flue gas. As the flue gas flows further up in the tower it is distributed to a set of parallel cyclonic droplet separator tubes. The gas first flows up around the outside of the tubes and then reverse flow to flow down through the inside to the tubes. A fixed vane at the top of each tube forces the gas to spin within the tube. Centrifugal force drive water droplet to the inside wall of the tube as the spinning gas flows down the tube. A weir at the bottom of each tube collects the water and returns it to the lower portion of the scrubber. Droplet free gas exists the bottom of each tube and enters the bottom of the stack.

Stage E - Exhaust to Atmosphere – The scrubber tower includes an integral stack sized to exhaust cleaned flue gas to the atmosphere. The stack height is typically driven by site and regulatory requirements. Outside atmospheric conditions often cool the stack wall and drives some water condensation on the inside wall. The stack dimeter and design allows condensed water to flow down the inside wall as flue gas flows up. The condensed water drains from the stack and is routed to lower portion of the scrubber. A specialized SDS termination device is used at the top the stack to boost the stack exist velocity for good plume dispersion.

Figure 6 – BELCO® Scrubber Tower at Bio Bio Refinery

Purge Treatment Unit (PTU) - Liquid purged from the scrubber section flows to the PTU. The collected catalyst fines are settled using an elevated clarifier. The gravity driven underflow from the clarifier is dewatered in a set of specialized filtering bins. Liquid drained from the bins is pumped back to the clarifier. The gravity driven overflow from the clarifier is oxidized in a set of atmospheric oxidation tower using air supplied by a set of blowers. A set of mixers enhance the air / liquid contact within the oxidation towers. The final liquid effluent from the last oxidation tower is low in COD and TSS. The PTU is shown in figure 7 and figure 8.

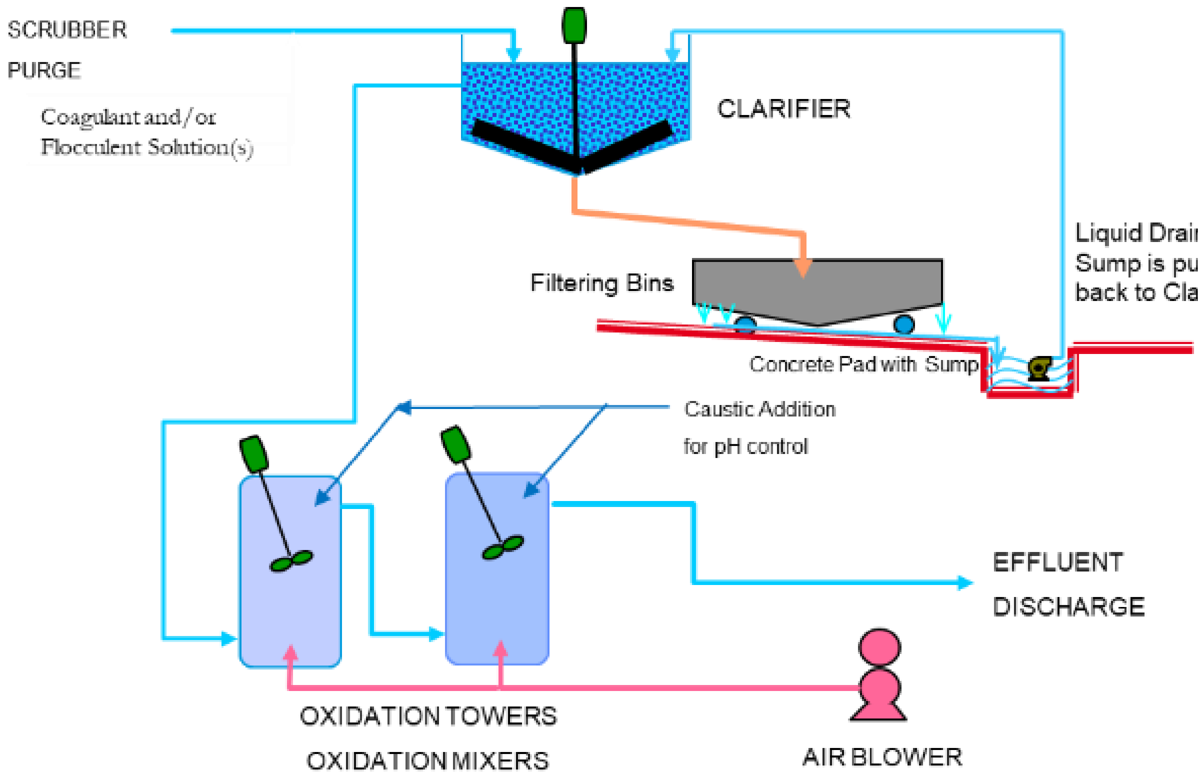

Figure 7 – BELCO® Purge Treatment Unit (PTU)

Figure 8 – BELCO® Purge Treatment Unit (PTU) at Bio Bio Refinery

Controlling FCCU Emissions at ENAP Refineries

The table in figure 9 summarizes the inlet flue gas design conditions to the BELCO® scrubber at each ENAP refinery. The inlet conditions are different for each. The flue gas rate and particulate loading are much higher for the Aconcagua refinery. The SO_2 inlet is much higher for the Bio Bio refinery.

Flue Gas to Scrubber	Units	Bio Bio Refinery	Aconcagua Refinery
Gas Flow	Nm3/hr wet kg/hr	48,314 - 88,576 63,637 – 116,676	59,012 - 129,826 77,301 – 170,063
Gas Temperature	Degree C	232 – 371	290 - 371
Particulate	mg/Nm3 dry	350 - 450	951 - 1,160
SO_2	ppmvd	1,615	550

Figure 9 – Inlet Flue Gas Design Conditions to Scrubbers

The table in figure 10 summarize the stack outlet design conditions from the BELCO® scrubber at each ENAP refinery. The SO_2 and particulate outlets concentrations (in mg/Nm3-dry and ppmvd) requirements are the same for each. The removal rates (in %) vary based on the different inlet concentrations at each refinery.

Flue Gas to Scrubber	Units	Bio Bio Refinery	Aconcagua Refinery
Particulate	mg/Nm3 dry	≤ 50 85.7%+ removal	≤ 50 94.7%+ removal
SO_2	ppmvd	≤ 50 96.9%+ removal	≤ 50 90.9%+ removal

Figure 10 - Stack Outlet Design Requirements

Emission testing at the Bio Bio refinery from September 2019 thru March 2021 is shown in figure 11 and demonstrates the performance to the BELCO® scrubber. Stack outlet concentrations are well below the original design requirements. The average particulate outlet is 14.4 mg/Nm3 dry compared to the design requirement of ≤ 50 mg/Nm3 dry. The average SO_2 outlet is 4.6 ppmvd compared to the design requirement of ≤ 50 ppmvd.

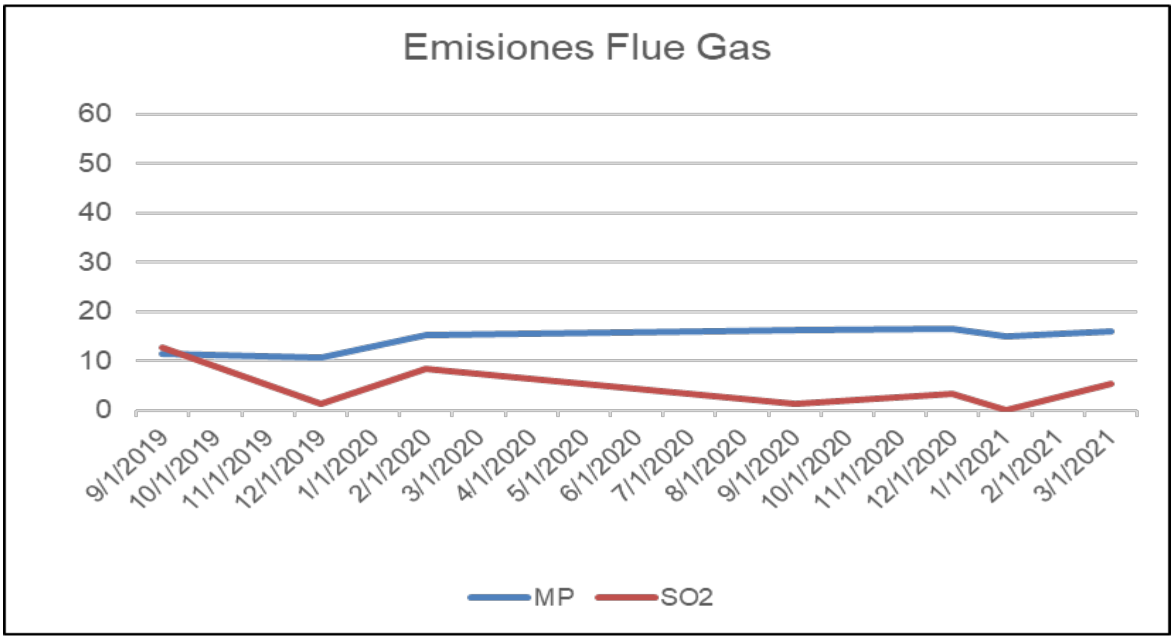

Figure 11 - Stack Outlet Testing Results

Based to the experience and performance on the FCCU at the Bio Bio refinery, the use of BELCO® scrubbing technology was selected by ENAP for the FCCU at the Aconcagua refinery. The design, engineering and fabrication are currently underway. Commissioning is expected by March 2023.

Conclusions

ENAP moved forward with major capital projects to reduce overall atmospheric emissions from both the Bio Bio Refinery and Aconcagua Refinery by installing wet gas scrubbers on the FCCUs. Emissions are now being successfully controlled on the FCCU at the Bio Bio Refinery to well below regulatory requirements. The selected BELCO® scrubbing system has performed well and continues to meet expectations two years after commissioning at the Bio Bio Refinery. A similar experience is expected for the Aconcagua Refinery as work progresses with the installation of a new BELCO® scrubbing system on the FCCU.

Refiners needing to control FCCU emissions have a variety of technologies and approaches to consider. BELCO® scrubbing is working well for ENAP and can work well for other refiners.

Brief CVs

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Claudio Hormazábal is a project director with more than 20 years' experience as a chemical engineer. He has been with ENAP for 16 years and has served as the Operational Team Leader for the coker complex project and the alkylation complex. He also served as the Coker/Alky Manager for 11 years. Mr. Hormazábal holds a BS degree in chemical engineering and an MBA from Adolfo Ibañez University.

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Scott Eagleson has worked on the application, design, and implementation of flue gas cleaning systems in oil refineries, industrial facilities and ships for over 30 years with Belco Technologies Corporation, an Elessent Clean Technologies company. This includes extensive work with BELCO® wet scrubbing and third stage separator (TSS) systems for fluid catalytic cracking units (FCCUs), as well as work on refinery fired heaters, boilers, incinerators, and sulfur recovery units (SRUs). He has authored and co-authored over 25 technical papers. He co-holds patents for flue gas cleaning technologies. Earlier in his career, he engineered rotary motion flexible shaft systems for a variety of medical, aerospace, automotive and industrial applications. Scott holds a BSME in Mechanical Engineering from Rutgers University, College of Engineering in New Jersey, USA.