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Operation and optimization of Carbon Capture Plant using BASF's OASE blue Technology

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Abstract

Solvay, a renowned producer of sodium carbonate and bicarbonate in Italy has taken measures to reduce its overall site CO₂ emissions and secure a stable supply of CO₂ for its chemical production. To achieve this, Solvay requested SIAD to install a carbon capture plant on its flue gas streams. The plant utilizes BASF's OASE[®] blue carbon capture process, which employs a specialty amine solvent formulation to produce a high purity CO₂ stream. After a construction period of 12 months by SIAD and TPI (Techno Project Industriale, an engineering company of SIAD Group), the plant was commissioned in June 2018. With a capacity of approximately 120 metric tons of gaseous and liquified CO₂ per day, the plant not only meets Solvay's own demand but also supplies high purity CO₂ to external customers.

The feed to the carbon capture plant comes from two major sources of CO₂ emissions. The larger flow of low pressure process off-gas stream from bicarbonate production (Stream A) with CO₂ concentration of around 17 vol.% (dry). The second source of flue gas (Stream B) has a CO₂ content of approximately 40 vol.% (dry) originated from lime kiln and coal combustion. The raw flue gases contain impurities such as calcium, sodium, and potassium compounds, including its corresponding carbonates, sulfur, oxides and particulates from upstream processes. These impurities are mostly removed through a filtration system, and a venturi scrubber on the Stream B stream while Stream A stream has a direct contact cooler upstream of capture process. The CO₂ capture section consists of an absorber with two mass transfer beds with an emission reduction zone that includes BASF's patented OASE[®] aerezone bed for aerosol removal. Once CO₂ is captured, the loaded solvent is regenerated in a stripper column heated by a steam system. The lean solvent is then circulated back into the absorber, and the CO₂ product is extracted from the top of the stripper with a purity greater than 99.9% (dry).

During the initial operation of the plant, the quality of the flue gas from both sources caused disruptions and negatively affected the overall performance of the carbon capture plant. Deposits of graphite, metal carbonate, sulfate and organic compounds were found in the solution and in equipment during the first turnaround inspection. A review of the pretreatment process revealed a higher than designed sulfur dioxide (SO₂) content as the main culprit. This resulted in insufficient removal efficiency and a rapid build-up of heat stable salt (HSS) in the OASE blue unit. Initial attempts to troubleshoot the venturi scrubber originally installed on the Stream A stream didn't show sufficient improvements. After a detailed review of the operational parameters in the CO₂ capture section, the venturi scrubber was replaced with a DCC on the Stream A stream to improve pretreatment efficiency. The unit was designed without an interstage cooler between the absorption beds, thus it operates by design at a relatively low lean amine loading to achieve the design removal efficiency. The combination of an increased strip steam / solvent-circulation-rate ratio and a high concentration of heat stable salts led to a higher amine make-up rate than the design value. The first optimization measure focused on changing the operational philosophy by increasing the solvent circulation rate above the design value while maintaining a constant reboiler duty. This had a positive effect on the OASE[®] blue solvent, as it improved the temperature profile inside the absorber by increasing the liquid / gas ratio. In fact, the reduced strip steam / solvent-circulation-rate ratio also resulted in lower amine degradation rate. In the effort to minimize operational cost, an ionic exchange reclaimer unit was also installed to decrease the concentration of heat stable salts, further reducing the amine make-up rate below the design value and improving the OASE[®] blue solvent efficiency over time.

Despite the challenges encountered, the carbon capture plant has demonstrated an economically attractive and transformative capture technology using BASF's OASE[®] blue technology. The systematic implementation of countermeasures and extensive operational experience by BASF, TPI, SIAD/SOLVAY joint effort in capture process have proved crucial in ensuring the long-term robustness and reliability of the plant's performance at this site.

Keywords: OASE blue; heat stable salts; flue gas; reclaimer; amine-based carbon capture; post combustion; operational philosophy; troubleshooting; simulation; high purity CO₂

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Nomenclature

MEA	Monoethanolamine
HSS	Heat Stable Salt
RCA	Root Cause Analysis
DCC	Direct Contact Cooler

1. Introduction

Solvay and SIAD have joined forces in a decarbonization project aimed at creating a synergy between industrial production needs and overall CO₂ emission reduction. The collaboration has formed an initiative that not only meets Solvay's production needs for sodium carbonate and bicarbonate, but also plays a vital role in reducing CO₂ emissions at Solvay's Rosignano site in Italy. The project serves a dual purpose in satisfying Solvay's demand for pure CO₂ supply, which is no longer linked to market shortages given that the CO₂ recovery rate surpassing the demand for pure bicarbonate production and at the same time contributes to the reduction of overall CO₂ emissions at the site. This project focuses on CO₂ capture from multiple flue gas sources using BASF OASE[®] blue technology. Figure 1 shows the block flow diagram for the facility after the retrofit with CO₂ capture unit.

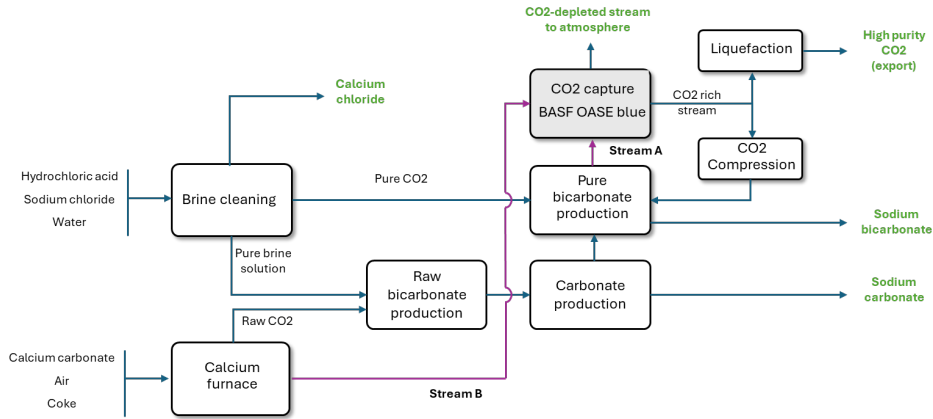


Figure 1 Block Flow Diagram at SIAD Rosignano

In 2016, TPI proposed to utilize an open art CO₂ process using MEA solvent. As the project progressed towards the end of engineering phase, TPI evaluated the use of OASE[®] blue technology due to cost and utilities limitations on site. This technology offers a lower solvent make up rate and regeneration energy resulting in substantial cost savings in project economics. Since the project had made significant progress in detailed engineering, BASF was only able to implement several design changes to further optimize existing MEA design. These changes include implementation of a different mass transfer packing type, inclusion of OASE aeroxone (dry bed configuration) with a single backwash design on top of the absorber, and re-simulation of the final process design using BASF's OASE[®] connect simulator. After a construction period lasting 12 months, the plant was successfully commissioned and began operation in June 2018.

2. Process Description

The CO₂ capture plant receives feed from two major sources, namely stream A and B. The Stream A has a larger flow of feed gas with a CO₂ concentration of approximately 17 vol.% (dry), while the Stream B flue gas stream has a CO₂ content of around 40 vol.% (dry). See Table 1 for the composition of each feed gas source. Both feed gas streams contain a variety of impurities such as calcium, sodium, potassium compounds, carbonates, sulfur-oxides, and particulates from upstream processes. To limit the amount of trace contaminants in the downstream capture unit, a filtration system and venturi scrubber were utilized on the Stream B stream, while a direct contact cooler (DCC) was installed on the Stream A stream. The combined stream then feeds into an amine-based carbon capture process for recovery of pure CO₂ with up to 99.9 mol% on a dry basis which then is used for increasing sodium bicarbonate production and CO₂ export upon liquefaction.

The BASF OASE blue unit, comprising of an absorber equipped with two mass transfer packing beds in which the CO₂ containing feed gas is absorbed chemically and is designed to achieve a minimum of 90% removal rate. Then, the treated gas from the upper absorber bed passes the first stage of the emission reduction section (OASE[®] aeroxone). This follows by a single water backwash section with pump-around loop, where the treated gas stream is further cooled before vented to the atmosphere.

The rich solvent undergoes a warm flashing step to remove inert components in the HP flash before going to the stripper column for solvent regeneration using low pressure steam system. The final product is extracted at the top of the stripper having CO₂ purity level exceeding 99.9 mol% on a dry basis. The regenerated solvent is then circulated back into the absorber for continuous operation with a slip stream going into a filtration loop. A reclaimer unit is also

tied into the lean solvent stream to effectively reclaim the solvent, thereby controlling the HSS content and reducing solvent make up in the unit.

Table 1 Flue gas condition upstream of carbon capture unit

Flue Gas Source	Unit	Stream B	Stream A
Flowrate	Nm ³ /hr	2,000	9,000
Temperature	°C	45 (Stream B before venturi scrubber) / 75 (Stream A before DCC)	
Pressure	bar(g)	0.04	0.3
Composition			
CO ₂	mol%	40 % (dry)	17 % (dry)
O ₂	mol%	1 (dry)	1.5 (dry)
N ₂	mol%	58 (dry)	81 (dry)
CO	mol%	1.97 (dry)	1.5 (dry)
NO _x	mg/Nm ³	300 (dry)	250 (dry)
SO _x	ppmv	< 2	5
H ₂ O	mol%	saturation	Saturation
Particles	mg/Nm ³	1	1

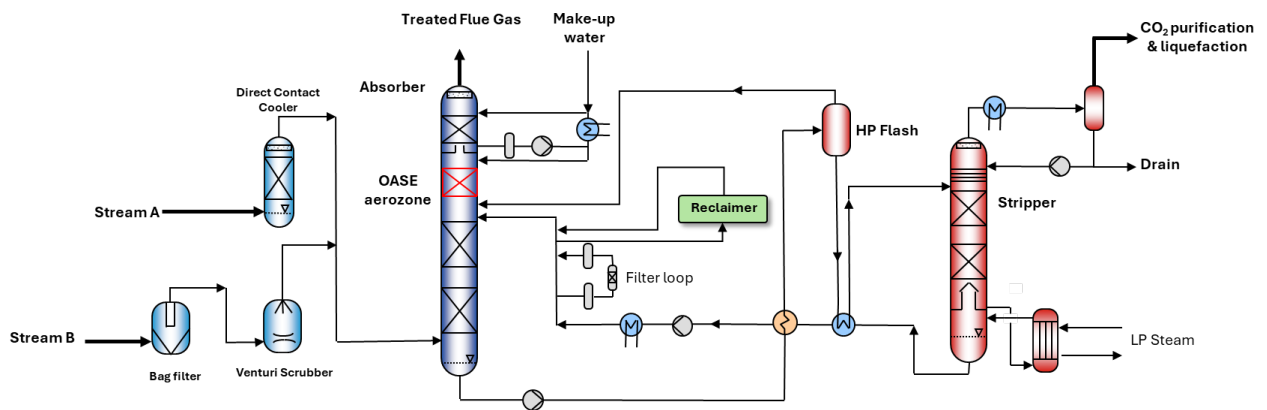


Figure 2 Simplified Diagram of BASF OASE blue at Rosignano Site

3. Operational Challenges

Since startup of the unit in 2018, there have been various challenges following the decision to switch from MEA solvent design to OASE[®] blue technology. This has led to a significant focus on addressing the following issues and implementing countermeasures on site.

- Particulates and SO₂ carryover
- High CO₂ in flue gas stream
- Solvent health and foaming

3.1 Particulate and SO₂ carryover

The presence of two different sources of feed gas adds a layer of complexity to the plant operation. This is because each source has a dedicated pre-treatment train to remove certain trace contaminants and protect amine solvent in the carbon capture process. During early years of operation, RCA confirmed the presence of particulates and SO₂ carryover as the main culprits. The RCA shed light on the inefficacy of the pre-treatment units in removing trace contaminants and particulates prior to its introduction into downstream process. This issue was particularly evident in Stream B flue gas source, which generated a variety of contaminants including carbonates, oxides, and chloride compounds. Back in 2018, the pretreatment unit in the Stream A stream only consisted of a venturi scrubber which proved to be insufficient, leading to particulates and SO₂ carryover into carbon capture process. This resulted in pressure drop increase across the solvent-solvent heat exchanger which subsequently led to plugging in the equipment and foaming occurrences in the absorber and stripper columns. Further observations from plant turnaround indicated brittle residues were also found in lean solvent pump strainers, the absorber bottom section, and in the solvent itself. Samples that were taken and tested contained graphite, metal carbonate, sulfate, and organic compounds sticking to the particulates (refer to Figure 3).

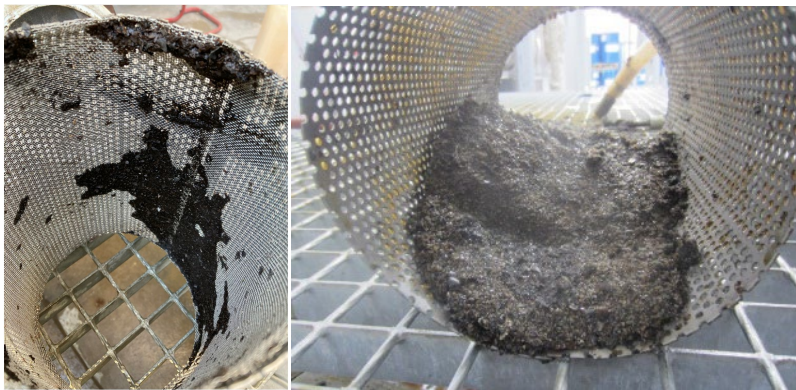


Figure 3 Brittle residues found during plant turnaround in pump strainer

During a major turnaround in 2021, the carbon capture unit was required to be flushed with hot water and acid solution followed by caustic treatment to effectively remove the accumulated debris under BASF supervision. To address the limited capability of the venturi scrubber in Stream A stream, DCC was implemented as a replacement and put into service in December 2019. Additionally, two grid mesh filters were also installed in the lean solvent stream downstream of the stripper to trap as much as possible the particulates carryover in the feed gas stream. With the implemented measures, carbon capture unit operation improved significantly.

3.2 High CO₂ in feed gas

This unit was initially designed for MEA technology. Thus, one of the main design draw backs encountered in this unit is inadequate mass transfer packing height in the absorber column. Since project execution was already at an advanced stage, there were little room for modification to optimize the process design. Consequently, post start-up optimization became necessary to improve absorption performance, especially considering the high CO₂ concentration in the feed gas which leads to greater exothermic effect in the absorber. Typically, a high CO₂ feed gas condition favours an interstage cooler in between the mass transfer sections in the absorber to allow for a better control of the temperature profile and higher solvent cyclic capacity to capture CO₂ in the feed. However, such configuration was not installed. To meet the treated gas specification and CO₂ removal rate, SIAD operation team initially operated the unit with a lower solvent lean loading compared to design value, leading to a higher reboiler duty. This resulted in

higher steam requirement leading to higher operational expenditure to maintain the unit. The combination of an increased strip steam to solvent circulation rate ratio and a high concentration of HSS further worsened the effect leading to a higher solvent make-up rate compared to the design value.

Considering the design circumstances, BASF recommended to change the operational philosophy of the carbon capture unit by increasing the solvent circulation rate above the design value while maintaining a constant reboiler duty. This adjustment required a new and larger pump capacity to be installed in the lean solvent stream and re-simulations of the process design to ensure optimum hydraulics of the new operating condition. The results of this change were favourable, and the temperature profile improved with increasing solvent circulation, resulting in a cooler temperature in the absorber column. When operating at a higher feed gas flow rate, decreasing solvent lean loading is done in conjunction with increasing the solvent circulation rate. This approach allows for more cost-effective operational strategy for the unit in the long run. Figure 4 shows the temperature profile with a slight bulge at the upper absorber bed recorded using thermal camera after the optimization step.

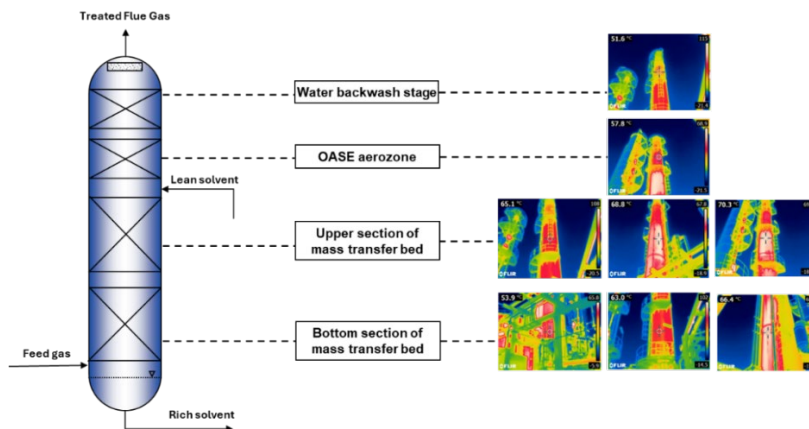


Figure 4 Temperature profile in the absorber captured by thermal camera

To further substantiate the data, BASF has validated these temperatures within $\pm 5\%$ variant with thermodynamic modelling by plotting the temperature profile across the absorber. The plotted temperature profile fits quite well with the data obtained from the thermal camera method. In fact, this profile is typical with no interstage cooler installed in between the mass transfer beds in absorber column as shown in Figure 5.

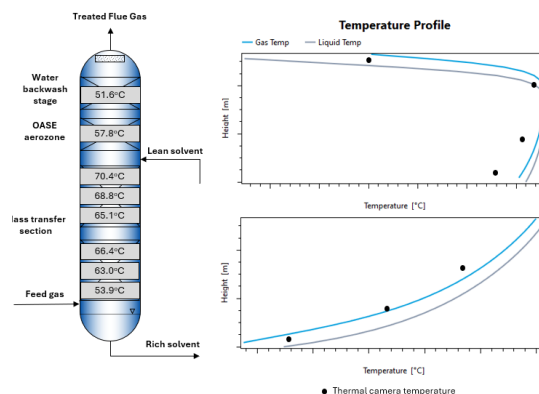


Figure 5 Temperature profile simulated by BASF confirmed thermal scan results conducted on site

3.3 Solvent health and foaming

Foaming presents a significant challenge for amine-based carbon capture plant. This issue is closely linked to the degradation products imposing limitations on feed gas rate and effectiveness of mass transfer rate. Like any other amine solvent, OASE blue solvent degradation occurs due to thermal stress and oxidative degradation from trace contaminants in the feed reacting with the solvent. Major degradation products formed are mostly consist of HSS including acetate, formate and oxalate. As a result of insufficient pre-treatment units during the initial phases of operation, there has been a higher-than-anticipated increase in the presence of HSS, with values reaching as high as 4.5 wt%. During this time, the only method to control solvent quality was through a bleed and feed strategy because no permanent reclaiming unit was integrated into the carbon capture process.

Furthermore, presence of particulate carryover in the feed gas exacerbated the situation, resulting in a series of foaming incidents within the process. Foaming occurrences were characterized by fluctuating levels in both absorber and stripper together with a rapid build-up of liquid level in the knock-out drum at the top of stripper. These occurrences were mitigated with shock dosage of silicon-based antifoam to stabilize the process and avoid further losses of solvent in the unit. BASF also recommended to operate the carbon filter bed on a continuous basis treating approximately 10% of cooled lean solvent. This allows for a more optimum removal of metal organic compounds functioning as precursors for HSS formation and reduces foaming tendency of the solvent.

In February 2023, SIAD installed a permanent ion-exchange unit supplied by MPR Services at the slipstream of lean amine solution line. The selection of ion-exchange technology was determined to be the most suitable at this site because of the highest amine recovery and minimal cost associated with hazardous waste disposal. The initial stage of the reclamation operation posed a significant challenge due to wastewater management. This limitation continues to have noticeable effect on the operational effectiveness of the reclamation unit, as it impedes the ability to maintain continuous operations. However, since the reclaiming unit start up, the solvent make up into the unit has decreased significantly (refer to Figure 6). Furthermore, the unit also observed a reduction in foaming tendencies in the solvent by maintaining a lower level of HSS in the solvent. SIAD continues to improve the operation of the reclaiming unit in accordance with its intended design and further reducing the operational cost of the unit.

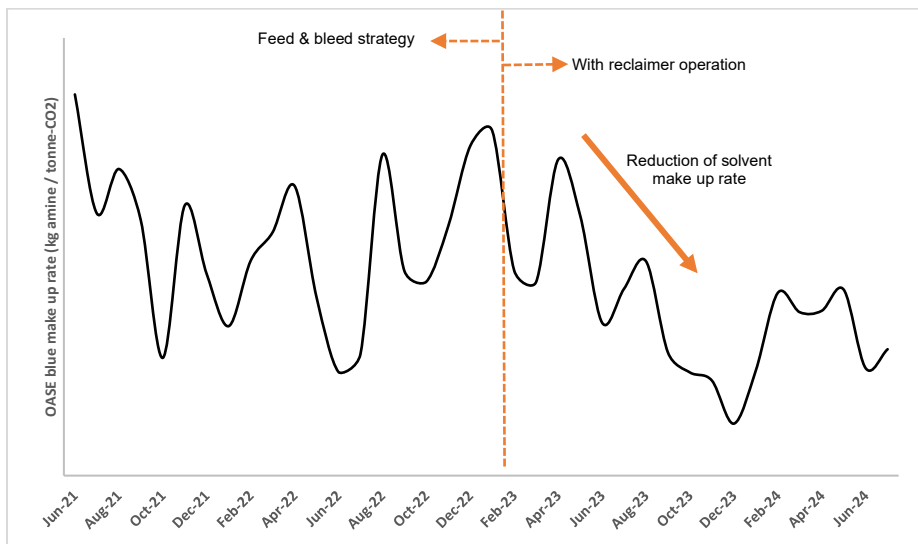


Figure 6 OASE blue solvent make up rate trend before and after reclaiming installation

4. Conclusion

Despite encountering numerous challenges, the carbon capture unit has effectively demonstrated resilience in operation utilizing BASF OASE® blue technology. The concerted efforts by all parties with implementation of countermeasures and significant operational experience by BASF and SIAD have proven to be instrumental in ensuring profitable and robust operation of the plant. Key challenges observed in the unit were particulate and SO₂ carryovers, high CO₂ concentration in the feed gas, and solvent health management. To address and optimize these issues, countermeasures include improvement of pretreatment unit line up and adjustment of operational strategy to improve carbon capture performance. Additionally, the installation of an ion-exchange unit has proven to reduce HSS levels in the solvent effectively, decreasing the solvent make up rate in the unit. This achievement is outstanding as OASE blue solvent continues to perform exceptionally well in achieving the desired removal rate and producing a high purity CO₂ product, even when operating with a heavily contaminated feed gas sources.