THE IMPORTANCE OF WATER TREATMENT IN SULFUR RECOVERY UNITS

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ABSTRACT

As the world moves towards more sustainable processes with minimum impact on the environment, plant designers are forced to investigate new ways of meeting stringent environmental regulations. Tight SO_2 emissions can be met using Sulfur Recovery Units (SRU) followed by caustic scrubbers, amine based tail gas treatment units (TGTU) or even biological conversion using the THIOPAQ® process. All technologies mentioned have effluent streams involving sulfur species. Even though a studied line-up can provide the most added value to the Client, it is not always possible to implement such process in case one of these effluent streams cannot be handled locally.

In addition, the shift in focus from a linear towards a circular economy, effluent streams are becoming of particular interest to plant designers and operators. Providing solutions which offer the end-user a fully functional line-up complying with modern emissions standards requires creativity and combining the best of two worlds. Jacobs Comprimo® together with Cool Separations B.V. has developed a solution for treatment of water effluent streams originating in SRUs which are difficult to handle by conventional water treatment solutions. In particular, water streams containing high levels of sulfates can be treated using an innovative process called Eutectic Freeze Crystallization (EFC). This process has been developed by Cool Separations for a variety of applications. Where conventional crystallization processes make use of boiling and evaporation or addition of chemicals to fully crystallize dissolved species, EFC makes use of freeze crystallization up to the eutectic point and in some cases, if so required, for the complete separation of salts and water beyond the eutectic point. This approach is far more efficient in terms of energy use which lowers operating costs. In addition, less hardware is required which saves investment costs and plot space. The benefits of this technology in combination with typical SRU effluent streams will be further explored in this article.

Introduction

Line-up considerations

In most refineries and gas plants, the sulfur recovery unit plays an integral role in meeting the environmental limitations of the facility. Depending on the environmental limitations, a technology licensor is typically involved in the design of these units. Depending on the technology selected, several effluent streams may have to be handled outside of the unit. Seemingly small, effluent streams such as water or a vent gas can require considerable attention in order to meet emissions requirements. With increasing interest in the reduction of effluent streams to the environment, plant operators are more and more forced to deal with any effluents streams.

Jacobs Comprimo® has experienced that the design offering the highest value to the Client may not necessarily be selected. Particularly when effluent streams seemingly cannot be handled on site, a proposed line-up may be cost-effective but incompatible with the Client's needs. Installation of dedicated treatment facilities is capital intensive adding complexity and increased plot space demand. As a result, the processing of the effluents produced by the lower cost technology could result in a much higher cost solution.

A worse scenario was encountered for a project well underway where the client discovered the inability to treat particular effluent streams causing an inconvenient situation. When licensors offer technology it seemingly provides a perfect fit with the intent to recover sulfur. Inadequate analysis of all the battery limits at the proposal phase may lead to surprises in the design phase of a project incurring delays and requiring further hardware. In order to overcome such issues, the creation of an all-inclusive solution by the technology suppliers could result in a project with an overall lowest cost and environmental footprint.

When considering providing a total solution rather than part of the solution requires a broader mindset outside the traditional boundaries of the field of technology for any technology supplier. This approach can also be found on a larger scale where the concept of a circular economy is being implemented. The use of resources generating materials or energy thereby creating waste is no longer valid. This linear way of thinking in the past has long since been overtaking by a drive towards more sustainable processes where waste materials become raw materials. This itself drives innovation in traditional production processes and new techniques for processing of these components. In addition, this development in turn is not only pushed from a desire to minimize emissions but also to reduce the operating costs of installations. As an example, the concept of 'Zero Liquid Discharge' does not only bring about additional costs in reducing emissions but brings about the re-use of water and minimizing the volume flow of waste streams. This can be quite valuable in remote locations where water is scarce. It also changes the way we perceive waste streams as this requirement motivates the valorization of waste streams. The re-use of water, reduction of the waste streams and recovery of resources results in a reduction of operational costs. It is logical to extend this philosophy to sulfur recovery units.

Effluent streams in Sulfur Recovery Units

In the figures below two commonly employed line-ups for Sulfur Recovery Units are presented. The catalytic conversion processes consisting of a Claus section, selective oxidation stage, with as industry standard the EUROCLAUS® and SUPERCLAUS® process, can achieve a sulfur recovery efficiency in the range of 99.0% – 99.6% [1][2] depending on the feed gas composition. The remaining 0.4% to 1.0% of sulfur species is incinerated and sent to the atmosphere as SO_2. For further reduction of the SO_2 emissions, a caustic scrubber can be installed downstream the incinerator. The absorbed SO_2 from the flue gas generates a sodium sulfate solution which can be treated at the site's waste water treatment plant (WWTP).

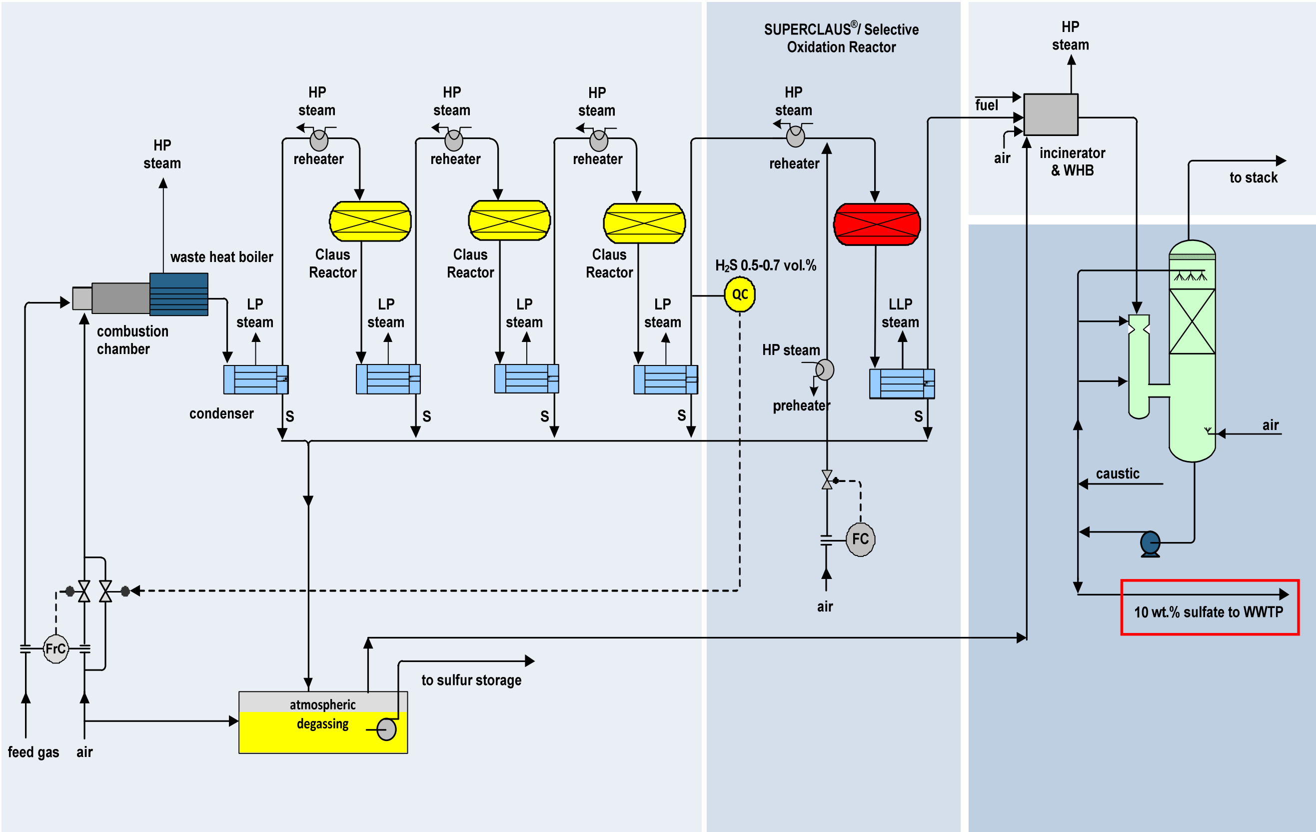

Figure 1: Line-up of SRU with SUPERCLAUS® + Caustic Scrubber

For sulfur recoveries greater than 99.5%, amine based tail gas treating units (TGTU) are the industry's standard. A typical line-up consists of a Claus section with two Claus reactor stages meeting up to 97% sulfur recovery. The remaining sulfur species in the gas are hydrogenated to H_2S which is captured by a selective amine based solvent. Quenching of the gas occurs upstream the Absorber stage in order to cool the gas and remove water originating from the Claus reaction. This condensed water contains dissolved species such as H_2S and SO_2 rendering it a sour water effluent stream typically treated in a sour water stripper column. A regenerator downstream the absorber regenerates the solvent releasing H_2S which recycled to the thermal stage in the beginning of the process. The treated gas is routed to the incinerator which converts remaining sulfur species to SO_2.

The configurations presented in Figure 1 and Figure 2 are cost-effective for sufficiently high sulfur capacities. Other technologies entering the traditional market include the biological THIOPAQ® technology which can handle sulfur capacities over 50 metric tons per day. Also this technology generates a sulfate effluent stream requiring further treatment. There are many other technologies found for lower sulfur capacities which will not be investigated in detail in this article. The line-ups discussed suffice to illustrate the effluent streams typically found within sulfur recovery units.

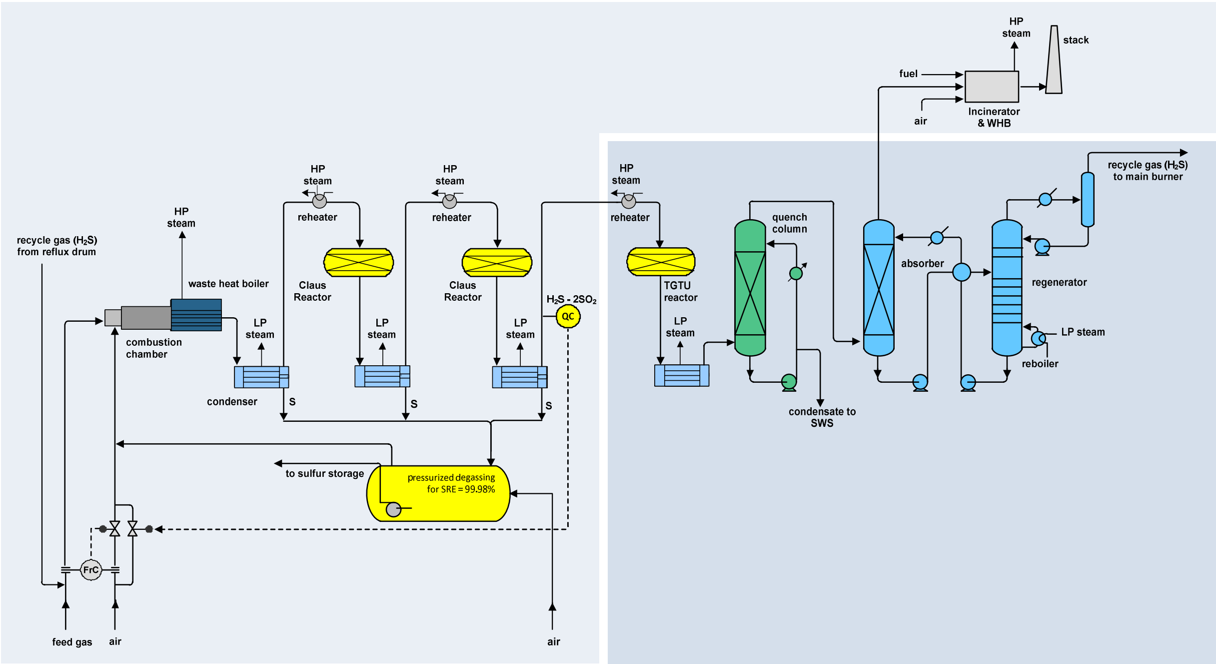

Figure 2: Typical SRU with amine based Tail Gas Treating technology

Typical effluent streams for sulfur recovery units include flue gas, sulfur storage tank vents, sour water containing H_2S and or ammonia, sulfate rich stream solutions from either caustic scrubbers or a biological SRU. Most gaseous effluents do not require additional attention but the different liquid streams need consideration for disposal. Sour water coming from a Quench Column in an amine based TGTU is typically treated in a sour water stripper. Most of the time such column is available on site and this stream is added to the feed. For new design a stand-alone dedicated stripper column is also implemented when required. The sulfate rich solutions found downstream Caustic Scrubbers or THIOPAQ® units can be treated by waste water treatment plants (WWTP). In Figure 1 the sulfate containing effluent stream of the Caustic Scrubber is highlighted in red.

Most refineries have a WWTP on site and these effluent streams add 1- 5% additional capacity by volume which can in general be accommodated without any issue. Although rich in sulfate, the dilution factor of the entire feed is sufficiently high such that these streams can be disposed of. There are several scenarios however where these liquid effluent streams can pose a problem:

- **Insufficient capacity or no WWTP on site** - in this case this effluent stream is to be processed off-site or a dedicated solution is required.
- **Too high sulfate content** – the local WWTP cannot treat the effluent stream or the concentration is too high for disposal to an external WWPT.
- **Remote location** – dedicated WWPT solutions are required in remote locations where the re-use of water can be of economic interest.

Insufficient or no water treatment processing capacity forces the plant operator to find a solution elsewhere. Strict compositional demands could limit processing in nearby facilities as was seen in a European gas plant where the nearby water treatment facility required a much lower sulfate content in the effluent stream.

Dilution could be a solution for lowering the sulfate content but would add operating costs and enlarge the overall waste stream. Removing species which are already concentrated is much easier. Preferably the components from the effluent stream such as sodium sulfate can be obtained in a pure state such that it can be disposed of more easily when serving as a raw material elsewhere. The industrial use of sodium sulfate can be found in the production of detergents, paper pulp industry (Kraft process) and in the manufacture of glass [3].

In the next chapter water treatment options for treating sulfate effluent streams will be investigated.

Water Treatment Options for Sulfur Recovery Units

Water Treatment Technologies

State of the art water treatment options for saline waste waters are numerous but suitability of these processes will be dependent on the feed composition and the requirements for solid waste and liquid waste handling after treatment [4].

Activated sludge (AS) is a process dealing with the treatment of sewage and industrial wastewaters. AS consists of three main components: an aeration tank, which serves as bio reactor; a settling tank for separation of AS solids and treated waste water. Atmospheric air is introduced to a mixture of screened industrial wastewater combined with organisms to develop a biological floc ("Activated Sludge"). AS is used for the following purposes:

- oxidizing carbonaceous matter: biological matter.
- oxidizing nitrogenous matter: mainly ammonium and nitrogen in biological materials.
- driving off entrained gases carbon dioxide, ammonia, nitrogen, etc.
- generating a biological floc that is easy to settle.
- generating a liquor low in dissolved or suspended material

AS systems can handle up to about 5 wt.% of salts in the feed like sulfates and chlorides. These systems are suitable to convert organic compounds into biomass but do not convert or separate salts fed to the process. Salts therefore leave an AS process with the waste sludge and treated water from the system rendering this technology unsuitable for treatment of a sodium sulfate rich effluent stream.

Anaerobic biological water treatment systems can handle up to about 1.5% of salt content in the feed. In these systems sulfate is reduced to sulfides which results in the metabolic inhibition i.e. poisoning of the necessary bacteria and the generation of high concentrations of gaseous H_2S, which means additional gas scrubber or adsorption beds are required to control gaseous sulfide emissions. Such a system is not preferred for treatment of small effluent streams in SRUs.

In case waste waters contain predominantly sodium sulfate and sodium bicarbonate/carbonate these salts could be removed by dosing milk of lime in order to precipitate calcium sulfate and carbonate as these compounds have low solubilities compared to sodium sulfate. E.g. the Cost Effective Sulfate Removal (CESR) process could get the salt level down to below 100 ppm in total. Despite the relatively low hardware investment i.e. if no sludge dewatering installation is required the operational costs will rapidly rise with increasing salt levels. Apart from the direct costs, the process creates a substantial amount of additional solid waste which adds on to the overall cost of this treatment process. For every ton of sulfate fed to the process about 800 kg of milk of lime is needed creating 1.8 ton of solid calcium sulfate waste. At a hydrated lime bulk price of 150 USD per ton this would add to the operational cost 120 USD per ton of sulfate.

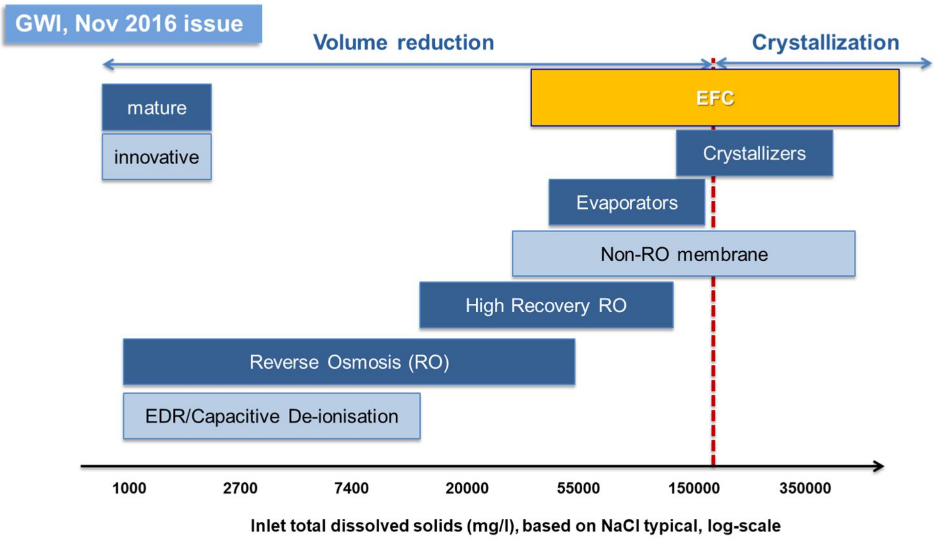

Figure 3: Volume reduction and crystallization technologies for saline solutions

Reverse Osmosis membrane filtration is limited in the feed salt concentrations it can handle. Feed salt concentrations of about 6 -10 wt.% depending on the specific salt type are already too high to consider direct RO treatment. A combination of the CESR process followed by RO would be technically viable but adds on to the cost per ton treated.

Another alternative is a two-stage treatment plant, e.g. Multi Effect Distillation(MED) or Mechanical Vapor Recompression(MVR) followed by Evaporative Crystallization in so called Forced Circulation Crystallizers (FCC) illustrated in Figure 4 [6]. The MED or MVR part evaporates water from the solution up to the maximum solubility of the main salts present at the boiling temperature avoiding crystallization of these components. In the FCC stage salt crystallization takes place allowing for the separation of salt and water. Apart from the fact that these systems are characterized by high CAPEX and high OPEX costs, mainly energy costs, also more waste is generated than the original feed by having to dose antiscalants avoiding scaling of the MED or MVR systems which causes downtime for cleaning. The FCC unit generates apart from clean water a completely mixed crystallized salt stream. Typical electrical energy consumption for these two stage systems are about 100 kWh per ton of waste water dependent on the feed composition. These systems are not easily scaled at these lower flow rates and therefore capital intensive.

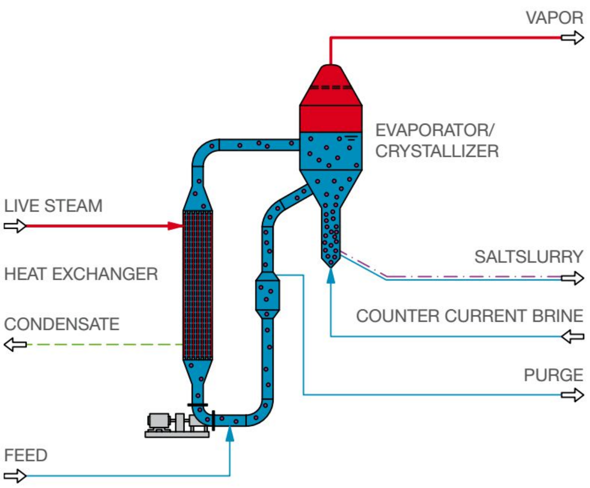

Figure 4: Forced Circulation Crystallizer (FCC)

Eutectic Freeze Crystallization

Another alternative is Cool Separation's Eutectic freeze crystallization (EFC) technology most suited for the treatment of highly concentrated saline to hypersaline aqueous streams. Either pure salts are separated from aqueous brine solutions or these brines are converted into pure water and pure crystallized solutes or salts all in one. As the heat of fusion of ice is six times less than the evaporation heat of water, the energy required to separate the water as ice is significantly less than that required for the separation by evaporation making EFC a highly energy efficient alternative. No antiscalants or corrosion resistant materials for equipment parts are required for this process.

The technology makes use of the difference in solubilities of various commonly known and widely appearing salt types in waste waters. Upon cooling, a number of these salts are characterized by a steep decline in solubility at temperatures unique for a particular salt making it possible to separate different types of dissolved salts up to the extent that these salts could even be reused. This phenomenon is quite different from the solubilities known at boiling temperature conditions.

A quite striking example is sodium sulfate which still has solubility in water of about 30 wt.% at boiling point. The solubility of this salt at about -1.5°C is only 4 wt.%. The result is that already from just an energy efficiency perspective it makes much more sense to cool a sodium sulfate containing stream for clean-up than evaporation. Depending on the actual sodium sulfate feed concentration, energy requirements for cooling per ton of feed waste water could be as low as only 20% or even less of the energy required for evaporation followed by evaporative crystallization for a complete separation of water and salt.

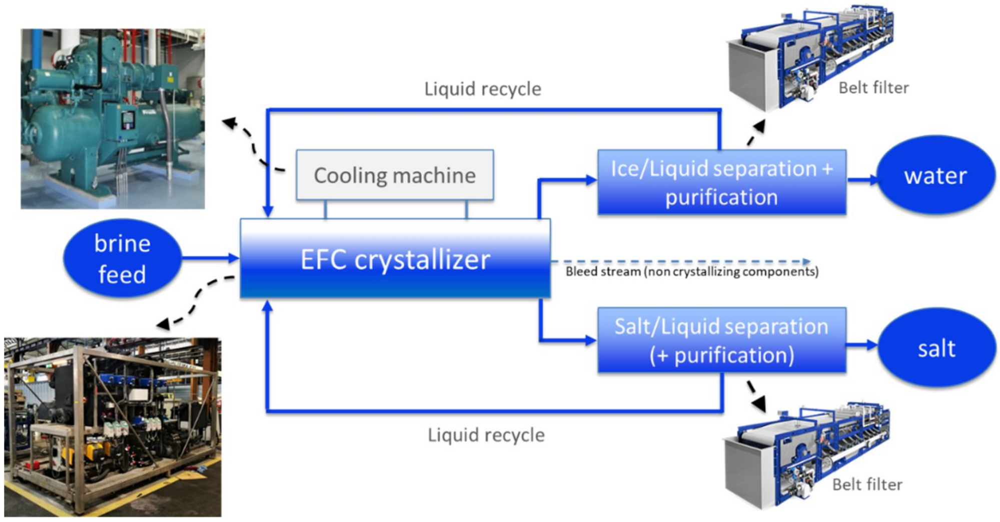

Figure 5: The Process Flow Diagram of the EFC process showing the main components

The EFC treatment plant

The main components of the EFC process shown in Figure 5 include the cooling machine indirectly cooling the EFC crystallizer, the EFC crystallizer and belt filters for separation of ice, salt and liquid. The EFC crystallizer consists of one to as many standard segments required to cool the brine to the required low temperature. Brine entering the crystallizer will be cooled to a temperature where salt and/or ice will crystallize. The crystallizer is constructed in such a way that maximum heat transfer is provided and no ice or salt scaling effects will hamper the heat transfer.

In the case a salt starts crystallizing first, salt crystals will deposit in the solution. This renders the water in the remaining brine or mother liquor to become purer. Once ice and salt start to crystallize simultaneously the system reached its eutectic point at a specific temperature and specific mother liquor composition depending on the type of salt. In theory, a 100% yield of both pure salt and water can be obtained in a binary system, which is one of the advantages of the EFC technology. Accumulation of highly soluble impurities can be controlled by small purge streams.

The sludge leaving the crystallizer is first separated in a salt rich phase and/or ice rich phase whereby the remaining brine phase is fed back to the crystallizer. As ice has a lower density than water the ice rich phase is easily separated from the salt phase having a higher density than water. The salt rich phase and the ice phase leaving the separator will now be filtered on separate vacuum belt filters. Here the ice and salt are further separated from adhering brine and washed to obtain the highest possible purity. The brine from the belt filters is fed back to the crystallizer. The cold from the streams leaving the process is recovered in the most efficient way possible.

EFC turnkey treatment plants in most cases can be supplied in containers or standard skids as presented in Figure 6. As this process is modularly scalable to a high extent, it creates a lot of flexibility for capacity expansions or capacity turn down. The off-site construction and testing reduces construction time on site.

Figure 6: Examples of modular EFC treatment skids

Case Studies

Case Study 1

The use of eutectic freeze crystallization was investigated for a caustic scrubber effluent of a plant located in China. In this case, the Client was looking for a solution to meet the stringent SO_2 emission specification of 50 mg/Nm^3 set by the authorities. As the existing technology applied in the plant was the SUPERCLAUS®

technology, Jacobs Comprimo® was consulted to offer the best technology to reduce the emissions down to the new required value. Installation of a caustic scrubber would result in the lowest investment cost for the Client. However, for this particular case, the sulfate content was too high for the local WTTP. The composition of the effluent stream is shown in Table 1.

Alternatively, an amine based TGTU could be considered. This would require a revamp of the installed selective oxidation reactor to a hydrogenation reactor and addition of the quench, absorber and regenerator section associated with a TGTU. As this option is more capital cost intensive than the addition of a caustic scrubber, finding a dedicated treatment option of the caustic scrubber effluent was evaluated first. Proven technologies capable of meeting the requirements included evaporative crystallization and eutectic freeze crystallization. For the evaporative crystallization solution, treatment of the 1.7 m^3/h (normal operation) effluent stream tends to be capital intensive due to the small size of the stream. For a forced circulation crystallization system, this capacity is at the low range.

Table 1: Typical Composition Case Study 1 Sulfate Containing Effluent Stream

Origin	Component	Concentration [wt.%]	Flow [m^3/h]
Caustic Scrubber	$NaSO_3/Na_2SO_4$ $NaHSO_3$ $NaHCO_3$	8 – 10 0.2 – 0.5 0.6 – 1.0	1.5 (normal operation)

Two types of evaporative techniques can be used for evaporative crystallization. Thermal evaporation requires steam for evaporation as well as cooling water for condensation of the evaporated water. With Mechanical Vapor Recompression technology more heat integration is possible by virtue of recovering the latent heat by pressurizing the evaporated water with a compressor. Installation costs are twice as high however for this option. For this revamp project investment costs were a big driver and the thermal evaporative option was selected using steam from the plant's grid for evaporation of the water in the effluent stream. This line-up consists out of a forced circulation evaporator. In the second stage crystallization occurs and the formed salts are removed using centrifuges.

The EFC units consists of a cooling section where both ice and salts are formed and separated simultaneously. Washing and drying occurs on belt filters after which the ice is recycled and the salts are collected.

The investment costs for this particular scenario are listed in Table 2 and the indexed data are presented in Figure 7. The figure clearly illustrates the lower investment costs when considering a Caustic Scrubber for this revamp situation compared to an amine based Tail Gas Treatment Unit. Even when considering an effluent treatment technology, the addition of a Caustic Scrubber remains competitive and cheaper. Plot space requirements for this scenario are also less considering installation of a single scrubber column and hardware required to treat the effluent stream compared to an amine based TGTU. Costs for the traditional evaporative technology are relatively high for a small effluent stream. The efficiency and scalability of Cool Separations' eutectic freeze crystallization allow for a fit for purpose solution with a higher added value for the client.

Table 2: Indexed CAPEX different options

Option	Index [-]
Caustic Scrubber addition	1.0

Revamp to SCOT	3.5
Caustic Scrubber & Evaporative Crystallization	1.42
Caustic Scrubber & Eutectic Freeze Crystallization	1.22

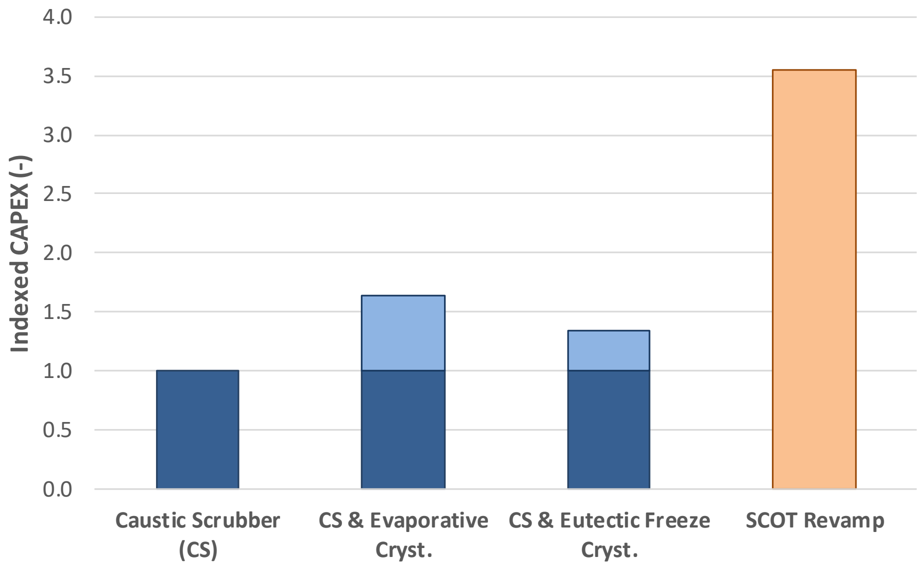

Figure 7: Indexed CAPEX for each scenario

In Figure 8, a comparison of the operational costs of an evaporative crystallizer making use of steam and cooling water compared to a eutectic freeze crystallizer is shown. Both figures are compared to the total operating costs of the evaporative technology. It shows that in particular the costs of LP steam and cooling water drive the operational costs for the evaporative crystallizer. In comparison the Eutectic Freeze Crystallizer does not consume steam and only a small amount of cooling water while also having a lower energy consumption.

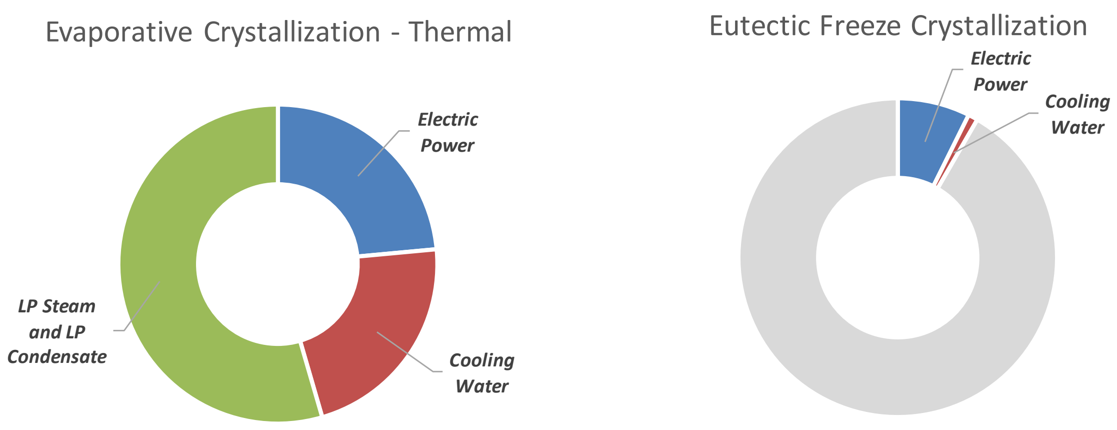

Figure 8: Comparison utility consumption vs evaporative crystallization

The numbers in this case study clearly illustrate the benefits of the Eutectic Freeze Crystallization technology compared to the alternative of an evaporative crystallizer. Lower investment and operational costs combined with a small footprint render the EFC process a valuable alternative to existing technologies for the treatment of the sulfate rich effluent stream

Case Study 2

For this particular case, a gas plant was designed in a remote and dry location. Total sulfur capacity equalled 15 T/D and a THIOPAQ® unit was designed for this project. No water treatment facility or fresh water supply was available on site. This meant that logistics of waste water would significantly add to the operating costs of the process and recovery of water had a high priority. Therefore, there was an incentive to recovery as much water as possible from the 1.5 m^3/h liquid effluent stream. This effluent stream apart from sulfate and carbonate species contained also dissolved solids such as biomass and elemental sulfur (Table 3). A line-up consisting of an ultra-filtration unit followed by an evaporative crystallizer consisting of two forced circulation crystallizers was compared to a eutectic freeze crystallization line-up. The back-purge and retentate of the ultrafiltration unit is recycled back to the main process. Both line-ups comply with the zero-liquid discharge concept and valorize the recycle of water and minimization of waste.

Table 3: Typical Composition Case Study 2 Sulfate Containing Effluent Stream

Origin	Component	Concentration [wt.%]	Flow [m^3/h]
THIOPAQ® effluent	Na_2SO_4 $S_2O_3^{2-}$ Biomass & sulfur (solids) TDS	5.0 0.5 0.2 2.0	2 (normal operation)

In Table 4, the main drivers for this case study are presented. For this project mechanical vapor recompression (MVR) was the preferred evaporative technology as this reduced consumption of LP steam and cooling water for the plant. Power supply was sufficiently available. The choice for this technology affects the installed costs which increases by virtue of compressors used for the overhead vapor. The MVR option proved to be twice as expensive as the EFC option. The benefit of MVR over a thermal evaporator is the re-use of heat for evaporation by using mechanical energy to condense the evaporated water. Exchanging heat with the feed stream allows for re-use of the heat. In a thermal system heat is used for evaporation as well as cooling duty for condensation of the steam. Therefore, for this technology only power is consumed. Overall power consumption for MVR is nearly twice as much compared to the EFC process.

Table 4: Case 2 Technology Option Characteristics

Treatment Option	CAPEX Indexed [-]	OPEX Indexed [-]	Water Recovery [%]
Evaporative Crystallization	1.0	1.0	89
Eutectic Freeze Crystallization	0.5	0.83	95

For the evaporative option salts crystals are filtered from the solution and dried with air from the surroundings before collected for transport. The EFC process of Cool Separations uses vacuum belt filters which recover more water which is recycled to the process.

This case study again shows the value the eutectic freeze crystallization process can offer to plant operators compared to existing technologies.

Outlook

When considering grass roots projects, the line-up with a Caustic Scrubber and dedicated effluent treatment can still result in a lower overall investment cost as illustrated in Figure 9 indicated with the red dot. This graph shows the overall investment costs as function of the sulfur recovery efficiency. For sulfur recovery efficiencies greater than 99.8%, an amine based TGTU provides typically a good solution. However, by adding a Caustic Scrubber to the Jacobs Comprimo SUPERCLAUS® technology, a new and cost-effective alternative can be provided. Even though the treatment of the liquid effluent stream on site requires additional hardware and investment costs, the case studies have illustrated the benefit it can have for the overall project costs. In particular, when a choice is to be made between a SUPERCLAUS®+Caustic Scrubber option and amine based TGTU type technology, the additional costs of an EFC unit are a lot less compared to the additional investment costs an amine based TGTU would bring about.

In case a sulfur specification of 50 ppmv in the stack is required an amine based TGTU such as LS SCOT could be considered. This is robust and proven technology but the difference compared to a SUPERCLAUS® + Caustic Scrubber Line-up meeting the same removal efficiency in terms of costs becomes even larger. For such cases performing a technology selection feasibility study is worthwhile.

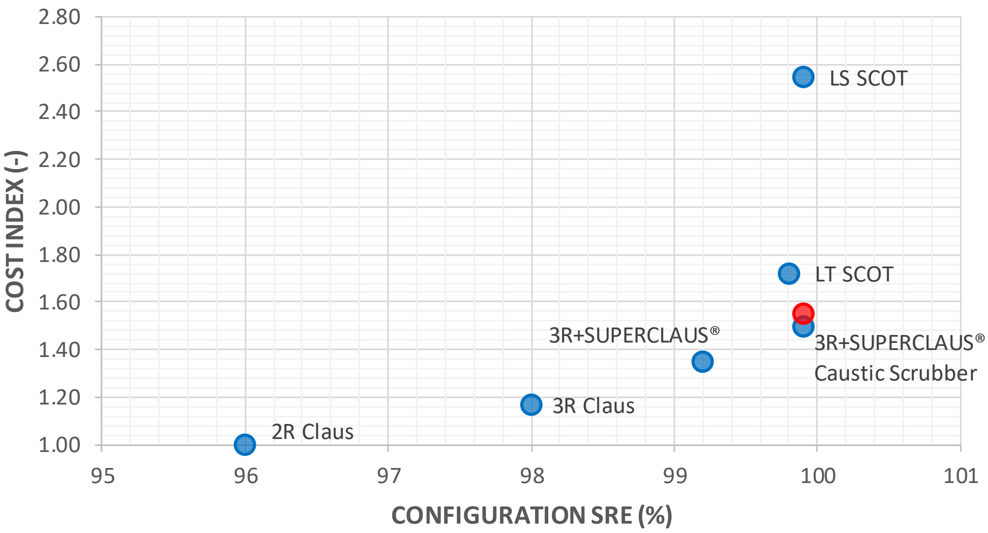

Figure 9: Overall investment costs vs configuration and SRE

The numbers presented in the case studies clearly illustrate the benefits of the Eutectic Freeze Crystallization technology compared to the alternative of an evaporative crystallizer. Lower investment and operational costs combined with a smaller footprint render the EFC process a valuable alternative to existing technologies for the treatment of the sulfate rich effluent stream. The advantage of scalability and modular design render this technology a perfect solution for treatment of sulfate rich streams in both grass roots and revamp situations.

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