Efficiency Up, Emissions Down

Matthew Viergutz, DuPont, USA, presents new ways to lower emissions and increase efficiency at sulfuric acid plants.

Sulfuric acid plants often operate for several decades, so industry investment decisions usually consider a combination of capital costs, operating costs, and long run emissions. Industry events, such as the HRS Roundtable, and symposiums at global conferences, such as CRU's Sulphur event, have shed significant light on the challenges facing producers today. MECS has long compiled feedback from the sulfuric acid industry to identify trends that can be used to drive long-term innovation. And while capital cost has always been important, the global sulfuric acid industry has increasingly pushed for improved energy efficiency, reduced emissions, and new ways to upgrade or replace its aging assets. In many countries, it is no longer acceptable to monitor emissions only during steady-state conditions. Producers have also identified an increasing need to manage emissions during transient conditions, such as startup, shutdown, and other upset periods, which is difficult with conventional sulfuric acid technology. Maintenance costs are also increasingly scrutinised as the industry tries to reduce its overall OPEX and, while overall industry trends are consistent globally, each sulfuric acid producer requires a custom plant design that meets local requirements. Therefore, it is no longer sufficient to provide a generic configuration. Each plant must be designed to guarantee freedom to operate while meeting the site's specific utility needs. With difficult trade-offs guiding the choices available to sulfuric acid producers, MECS foresaw that a novel approach would be required to simultaneously improve emissions and reduce CAPEX and OPEX.

MECS has licensed its ClausMaster™ regenerative scrubbing technology for many years in a variety of applications. Figure 1 shows how this technology uses consecutive absorption/regeneration stages with a closed loop solvent to absorb and regenerate SO_2 gas.

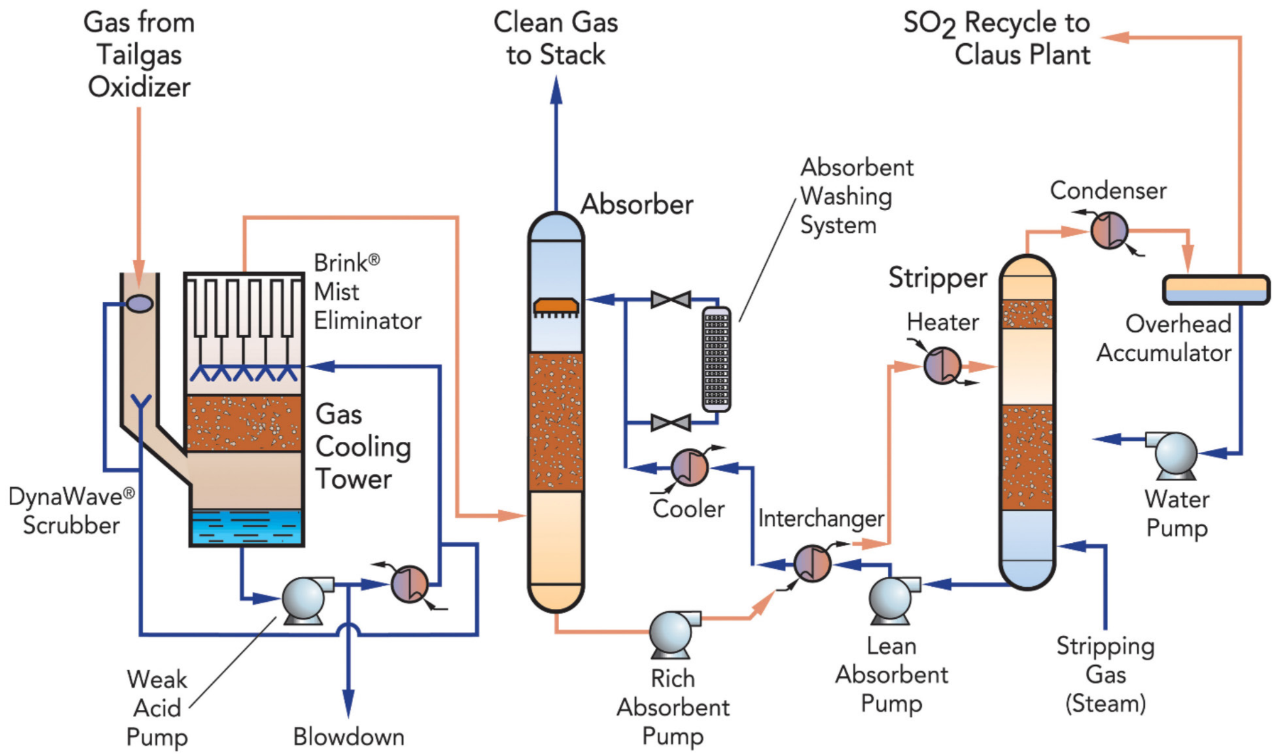

Figure 1. ClausMaster™ process.

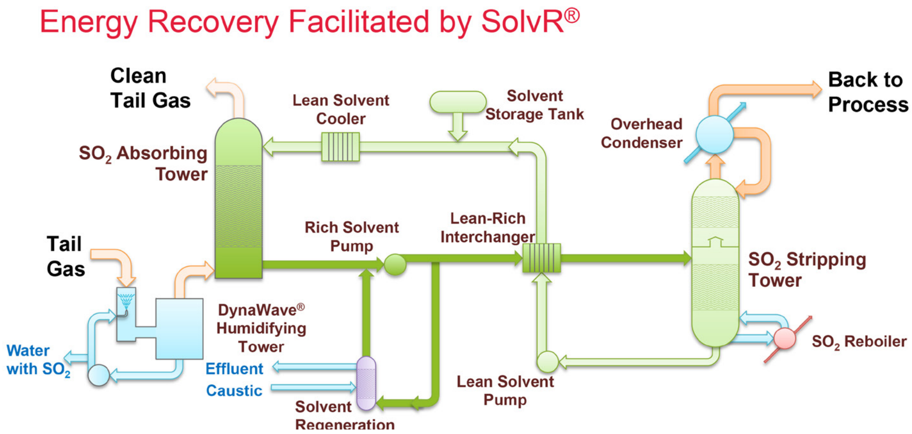

Figure 2. SolvR® process.

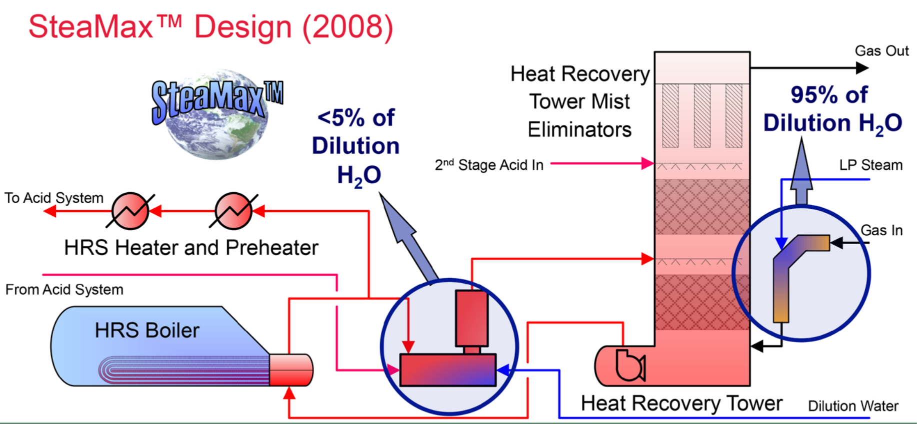

Figure 3. SteaMax™.

While the ClausMaster technology had successfully demonstrated the ability to remove SO_2 from gaseous waste streams, it did so with a few relatively critical drawbacks. In the late 2000s, MECS reviewed the technology's most glaring limitations and set out to develop an improved solvent that would be readily available worldwide, would use lower cost construction materials, and would be designed to operate in the 'sweet spot' of tailgas emissions from a single absorption sulfuric acid plant. This effort began with an extensive search of physical property databases to identify families of solvents that met the rigid performance criteria. Next, a worldwide intellectual property review led to a determination that preliminary work would result in the development of a technology that was both free from infringement risk and also could be patented. Pilot plant tests verified the performance of the solvent in both SO_2 removal efficiency and resistance to corrosion. The upgraded regenerative technology was named SolvR® and was ready for commercialisation.

New technology

SolvR technology, first commercialised in 2014 at a sulfur burning plant in the US, follows the same principles of unit operations as the ClausMaster process. As shown in Figure 2, tailgas from a sulfuric acid plant is adiabatically hydrated in a DynaWave® scrubber and flows into a countercurrent absorbing column, where SO_2 is absorbed into a circulating flow of solvent.

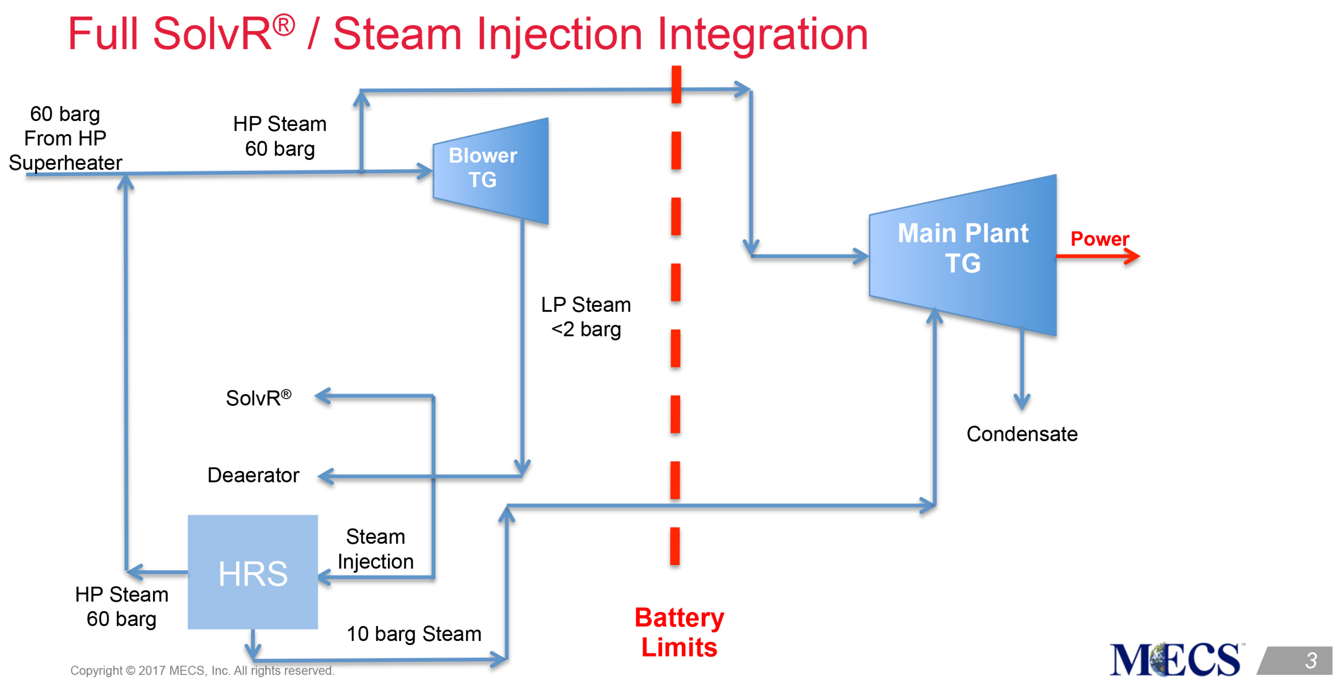

Figure 4. MAX3™ heat integration.

Clean gas exits the absorber at the top, and the rich solvent is pumped to a stripping tower which removes SO_2 by steam stripping. SO_2 is recycled to the front end of the sulfuric acid process, and lean solvent is pumped to the top of the absorbing tower. MECS also provides a solvent regeneration system to remove sulfates that will accumulate over time. Effluent from the SolvR system is an aqueous sodium sulfate solution that can either be sent to battery limits or concentrated to produce higher grades of sodium salt. It should be noted that SolvR is an upgrade over ClausMaster for several reasons. Firstly, the SolvR solvent does not require unique stainless steel materials, leading to a significant reduction in the cost of the system. Further, it is readily available and is lower cost than other regenerative solvents used to remove SO_2. Finally, steam consumption is lower than in the ClausMaster process and, while the SolvR system is a net consumer of energy, steam injection can be used to closely integrate heat recovery between the SolvR and the acid plant in a breakthrough way.

Steam injection

Steam injection offers an economically advantageous method for maintaining concentration control in the heat recovery system (HRS) acid system. A portion of the water required for concentration control is provided through the steam injection vessel, and the remainder is provided in the HRS diluter. Low pressure steam is injected into the process gas in a steam injection chamber upstream of the heat recovery tower. Since the overall enthalpy of the water fed to the HRS is higher when steam is used, the latent heat from condensation boosts generation of HRS steam compared to HRS designed without steam injection. Effectively, steam injection upgrades low pressure steam that would otherwise be vented to the atmosphere. Utilising steam instead of dilution water has a few additional benefits that are not related to energy recovery. Firstly, the mechanical energy load on the diluter is greatly reduced, minimising vibration and other mechanical stresses on the piping system. Secondly, less acid circulation is required in the HRS tower because the concentration rise is lower, reducing the power consumption in the plant. Finally, because less acid is circulated in the HRS, all HRS equipment becomes smaller, reducing the capital cost of the plant.

Approximately eight years ago, MECS introduced SteaMax™ (Figure 3). In SteaMax HRS designs, the company uses an even higher steam to liquid water ratio for dilution, approaching operation with little or no liquid water for dilution. This configuration multiplies the enthalpy effect of conventional steam injection, allowing most plants to realise gains in absorption heat recovery of 20 – 30% over a conventional HRS with steam injection. But the most important benefit of SteaMax was unrealisable until the development of SolvR. Combining these two technologies leads to a new process: MAX3™.

A new process

Combining a single absorption sulfuric acid plant with SolvR leads to both gains and losses with respect to heat integration. Additional heat is recovered because the interpass heat exchangers are not required in a single absorption sulfuric acid plant. However, SolvR consumes both low pressure steam and cooling water, so is there a way to integrate all of these technologies to offset utilities required in SolvR?

To solve this problem, MECS design engineers first started with the principle that, essentially, each kilogram of low pressure steam fed to the steam injection chamber is upgraded to approximately 10 barg steam in the HRS. While this is true in theory, it has been difficult to achieve in practice because few sulfuric acid plants have excess 2 barg steam available for steam injection. Furthermore, the requirement for SolvR to consume 2 barg steam would seem to leave no opportunity for integration, but it is these two fundamental challenges that the MAX3 process overcomes

Table 1. Case study: 3400 metric tpd

Export/import	Conventional double absorption	Double absorption with HRS™	MAX3 with steam injection
Total export steam	176 000 kg/hr	215 000 kg/hr	205 000 kg/hr
HP steam export (60 barg, 500˚C)	132 000 kg/hr	132 000 kg/hr	179 000 kg/hr
IP steam export (5 barg, saturated)	0	67 000 kg/hr	26 000 kg/hr
LP steam export (2 barg, saturated)	44 000 kg/hr	16 000 kg/hr	0
SO_2 emissions	400 ppmv	400 ppmv	30 ppmv
Cooling water	6500 m^3/hr	3500 m^3/hr	2700 m^3/hr
Power use	2400 kW	2400 kW	2300 kW
Effluent (1% Na_2SO_4)	0	0	15 m^3/hr
Solvent regen	0	0	US$575 000/yr

to simultaneously reduce capital cost, operating cost, and emissions. Figure 4 shows a flowsketch of a turbine-driven main gas blower that produces 2 barg steam – inside the acid plant battery limits – which can feed the SolvR and can be upgraded to either intermediate pressure steam or high pressure steam in the HRS.

This heat integration flow scheme overcomes common shortages of 2 barg steam while upgrading this low grade energy source to higher value steam via SteaMax. Table 1 shows a case study comparing battery limit conditions of conventional, HRS, and MAX3 processes.

By integrating the SolvR and SteaMax systems, MECS shifts a portion of the steam produced in an HRS acid plant to high pressure steam. The MAX3 process is able to achieve this upgrade at emission levels that are an order of magnitude lower than conventional designs. If a producer planned to build a sulfuric acid plant with an SO_2 emission level higher than 30 ppmv, MAX3 would recover even more energy than as shown in Table 1.

MECS sold its first MAX3 plant in 2015 and its second in 2016, and in both cases successfully leveraged the flexibility of the SolvR regenerative system to design unique configurations for each customer that minimised costly utilities and maximised profitable exports on a site-specific basis. These custom designs would not have been possible using conventional acid plant technology, which is typically restricted to a single configuration with only the ability to make small modifications. In moving the industry towards more customisation, sulfuric acid producers should be offered the flexibility to evaluate numerous designs so that each new acid plant can be as profitable as possible. WF