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small scale plants for affordable, local solutions

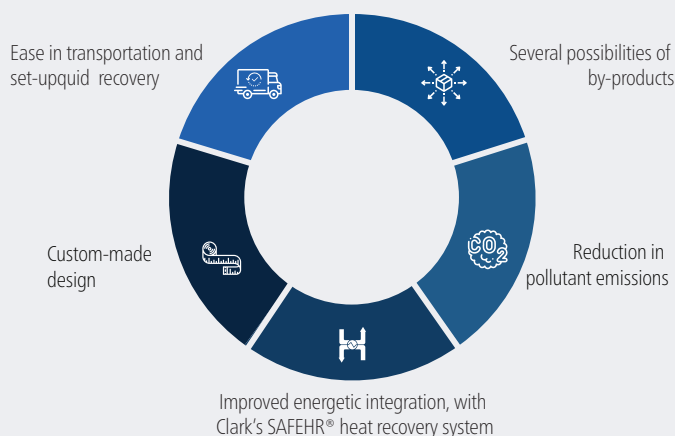
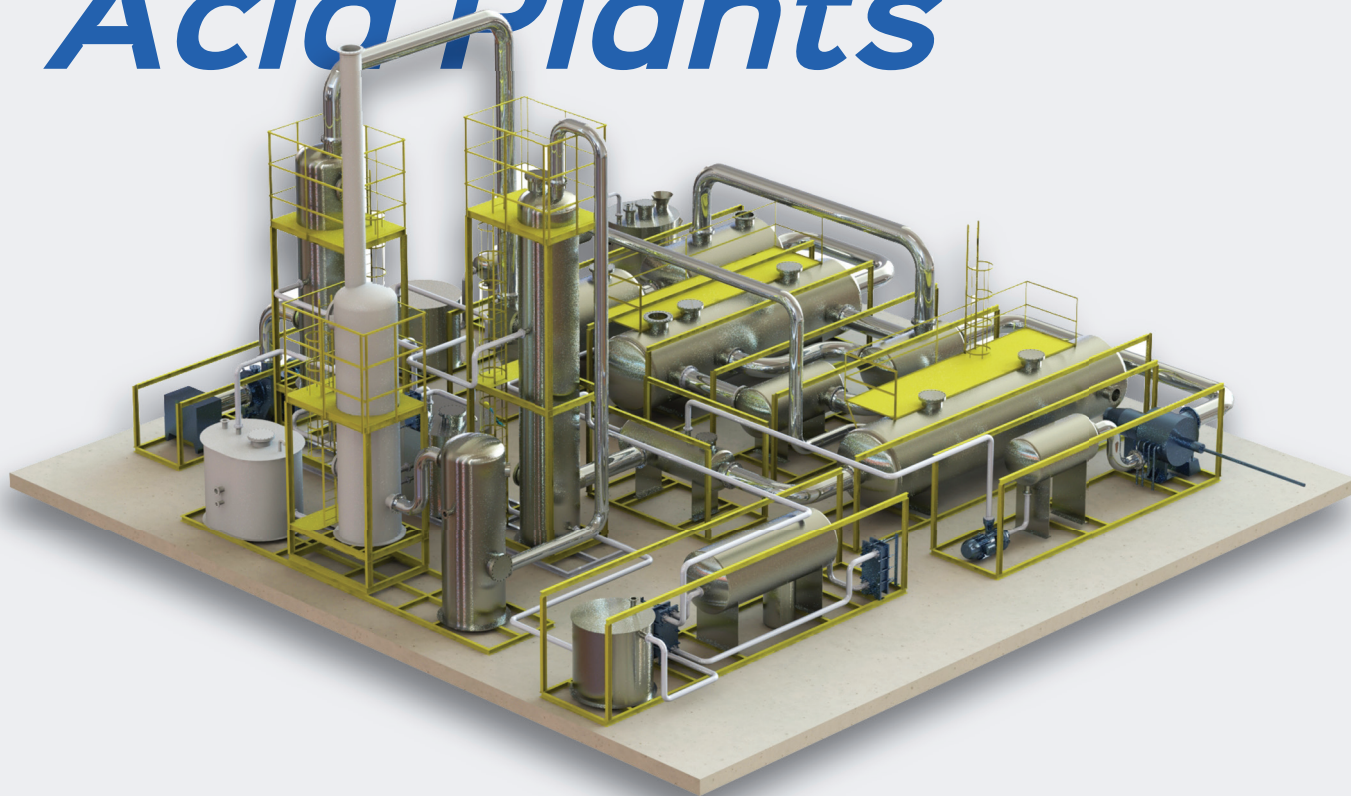


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Modular Sulfuric Acid Plants



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Self-Sufficiency Technology

Small and mid size consumers are often dependent on large integrated complexes and trading supply centers for their sulfuric acid.

Besides the strong dependency created by the a third part supplier, logistics and cost forecasting are usually additional issues.

In house acid production breaks the dependency, simplifies logistics and improve costs predictability.

Clark Solutions modular sulfuric acid plants help small and mid size acid consumers to address these issues. Sulphur burning plants form SO biometric tons per day will supply price competitive acid and energy.

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Modular Acid Plants

Victor Avila Garcia, Victor H. Machida, Vitor A. Sturm, Eduardo H. R. A. de Almeida, Bruno B. Ferraro, Nelson P. Clark, Clark Solutions, Brazil, consider a new heat recovery system for modular acid plants.

Draft

Developing on demand, small-scale sulfuric acid production facilities has become increasingly attractive to small and medium-scale consumers. Many have their operational performance impaired due to logistical complications, such as difficulty accessing large production and supply centres, the costs of transporting and storing acid, due to the nonconversion of effluents into products of significant industrial and/or economic value.

Companies that incorporate sulfuric acid into their production can look forward to obtaining greater productive autonomy or more efficient effluent disposal by resorting to modular plants. These are factories that focus on ease of installation and incorporate either or both sulfur in its elemental state, or in the form of gaseous oxides, sulfur dioxide (SO₂) and sulfur trioxide (SO₃).

Understanding the technology

Modular acid plants are designed for mobility, and processual versatility and simplicity of installation. This technology aims to offer a strategic option to industries that incorporate sulfuric acid as raw material or high value production asset. It guarantees supply reliability, price predictability, and minimises transport risks and any associated operational expenditures.

Although the design is custom-made to be a means of withstanding customer requirements and limitations, modular plants follow an overall schematic. They are suited to improved energetic integration, efficient conversion, proper effluent treatment and generation of interesting byproducts. As such, several technologies for gaseous effluent treatment are available to perform SO₂ removal with high efficiency and potentially create the opportunity to develop new products. These include:

- Tail gas scrubbing single absorption system: non-reacted SO₂ is retained by a solvent and a byproduct is formed. Usually, such solvents are hydrogen peroxide, where diluted sulfuric acid is formed, caustic soda, from which sodium sulfite is generated, and an ammonium-based solvent, allowing synthesis of ammonium sulfite and bisulfite.
- Single absorption with regenerative system: SO₂ can be recovered and recycled to the plant inlet through an absorbing fluid that passes through a cyclic system of absorption and stripping of SO₂.
- Double absorption: where energy and by-products are less important or non-integrable.

The modular sulfuric acid plant is built into several modules, each for a functioning step of the acid synthesis process. These structures are arranged in skids, which are interconnected after

the setup and designed with 40 ft. standard container dimensions or smaller to allow for easy transportation. This arrangement grants versatility in installing and decommissioning according to production demands and within logistic planning. In case of total shutdown, the modular plant can be transported to a different productive unit.¹

Modular plant layout

As an example, a modular plant that utilises single-absorption stage and a tail gas scrubbing system is shown in Figure 1. It was developed for a mining company that incorporates sulfuric acid in its productive scale. The factory unit consists of:

1. Solid sulfur melting and filtering.
2. Sulfur burning furnace and main boiler: generation of SO_2 and availability of low or high pressure steam produced in the waste heat boiler, for energy generation or onsite operations.
3. Catalytic converters 1 and 2: gases from the furnace are admitted on a horizontal two-passes converter, designed with the assistance of computerised fluid dynamics.
4. Catalytic converters 3 and 4 – these are fed gases from converters 1.

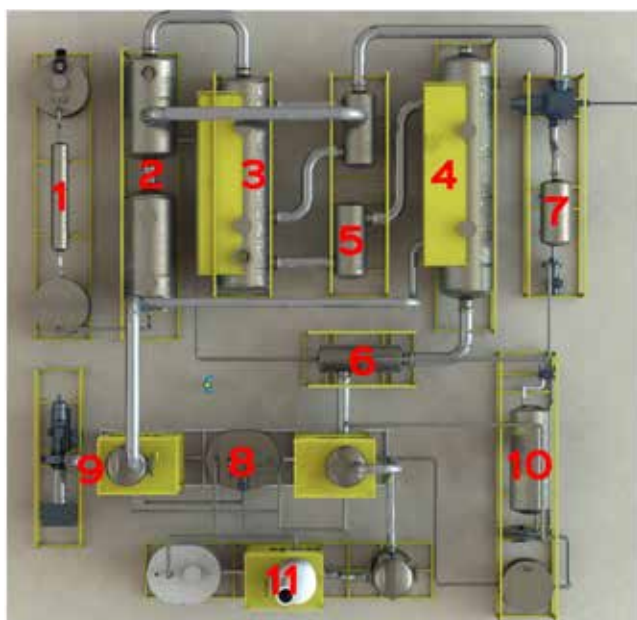


Figure 1. Modular plant arrangement.

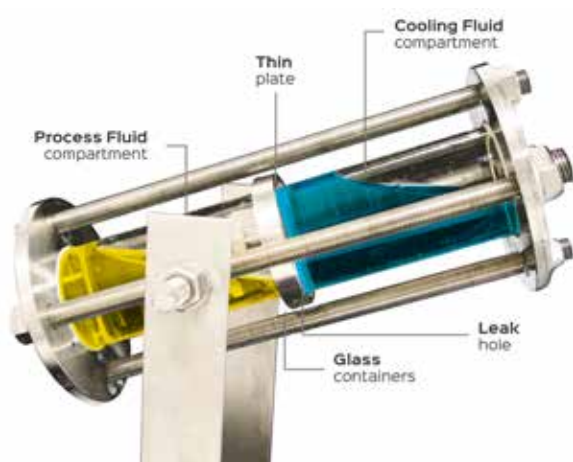


Figure 2. Skid for energy recovery in a modular acid plant.

5. Steam systems 1: heat generated in SO_2 conversion is recovered using the boiler feed water (BFW) or the boiler steam, using different arrangements of economisers, superheaters and secondary boilers.
6. Steam systems 2: a second skid with steam systems is usually provided when more exchanger area is required.
7. Electricity generator: steam is fed into a steam turbine, providing electrical power. The skid contains the complete co-gen cycle with deaerator and condensator.
8. Sulfuric acid skid: this consists of a drying tower, an absorption tower and a combined acid tank. The drying tower removes all water content from inlet air, which is fed to the furnace. In the absorption tower, SO_3 comes into contact with a counter-current, which recirculates sulfuric acid, reacts with remaining water and further increases its concentration.
9. Main blower: this skid consists of a blower that feeds the plant.
10. Tail-gas scrubbing system: non-converted SO_2 is directed at a gas scrubber tower, allowing its clean emission to the atmosphere and generation of byproducts.

The sulfuric acid industry has largely followed the dual absorption route which, while increasing the conversion of SO_2 to SO_3 from 96 – 97% to 99.6 – 99.7%, reduced SO_2 emissions amid environmental pressures. This gain was almost exclusively due to increased energy consumption.

The choice of a double or single-absorption system is of utmost importance. While the former has been the preferred option due to its higher conversion rate and superior emission control, rising energy prices in the late 20th and early 21st centuries made single-absorption plants with SO_2 regeneration systems or stack gas scrubbing a very interesting route. This was done in such way that modern catalytic converters and technological developments in tower internals gradually allowed single-absorption to replace double.

To assemble a double-absorption system, the installation of a second absorption tower and two gas-gas heat exchangers is required. This greatly raises processual expenditures in capital, operation, maintenance and installation of adjacent equipment such as instrumentation, pumps and acid coolers.

The single-absorption method has been the favoured design option in modular acid plants, on account of its low costs, greater processual reliability and safety, higher operational margin and easier start-up.

Safe heat recovery

The furnace and catalytic bed conversion stages are the main sources of heat in a contact process sulfur burning plant – which is used to produce steam using boiler, superheater and economiser systems. A substantial amount of heat is generated during the SO_3 absorption steps, for the recovery of which several systems have been developed, which represents nearly 35% of the plant's total generated energy and is usually rejected to cooling water in conventional arrangements. These systems for heat recovery succeed in raising the circulating absorption acid temperatures to values that, when cooled by a boiler, can generate medium pressure steam.

However, high temperature acid is extremely corrosive, and improper maintenance or anti-corrosion systems may induce leaks or contamination inside heat exchangers. The contact between hot sulfuric acid and pressurised water further accelerates dilution-

induced corrosion damages, greatly increases temperature, and generates explosively hazardous hydrogen gas. Also, in case of failure, general plant shutdown is required. This incurs significant production losses in sulfuric acid, high and low pressure steam and, eventually, shutdown of the integrated plants.

Amid concerns regarding operational hazards, Clark Solutions has developed SAFEHR®, a heat recovery system focused on safety, whose design relies on an intermediate circuit between the acid cooling and the steam generation systems, as to avoid contact between water and acid.

The system operates with concentrated acid, which is utilised to absorb SO₃ in the absorption tower. The acid is heated then cooled in a heat exchanger with an inert fluid, CSF, which is inert to, and immiscible with, acid and water. Therefore, in the event of an acid leak into the intermediate fluid system, there is no risk of producing dilute acid and hydrogen gas. As there is neither dilution nor heating of the acid, the leak is not self-catalysed and will not accelerate as it normally would in conventional systems. These properties allow programmed decisions on when and how to shutdown. The system also includes a coalescer and controlled drainage system from which acid-fluid or water-fluid separation occurs, avoiding the liability of losing intermediate fluid to the process.

The company's heat recovery system can be set up accordingly to the customer's interest in byproduct generation. Some options include:

- Cooling water system solely for concerns regarding operational safety.
- BFW: pre-heating water for the main boiler. This arrangement allows production of high-pressure steam, while conventional heat recovery systems would allow medium-pressure steam only.
- Medium-pressure steam generation, directly from the system's heat exchanger.
- Multi-user stand-alone system: a combination of the aforementioned technologies, used for district water heating, electrolyte heating and other options.

In order to observe a practical comparison between a typical heat recovery system and SAFEHR, a test apparatus was used to determine their corrosion rates in two distinct arrangements. The first is a typical water/sulfuric acid system, in which a dangerous exothermic reaction takes place and can cause plant emergency shutdown. The second is from the system's technology and no corrosion or reaction can be detected, the results of which are shown in Table 1.

Case study: acid plant in mining company

A small acid consumer in Brazil chose to build its own sulfuric acid plant, instead of purchasing from suppliers due to the plant's remote location. The company acquired a 150 000 tpd plant to produce acid from both sulfur burning and effluent gases generated in calcination furnaces, which were contaminated with large amounts of SO₂ and SO₃.

The raw material sources for sulfuric acid synthesis are elemental sulfur and effluent gases, which reach the factory unit at a temperature of 360°C and contain approximately 4.3% SO₂, 2.7% SO₃ and 2.1% H₂O. Once the solid sulfur is melted and filtrated, it is directed to the furnace where the gaseous stream also enters the system. This process increases SO₂ content to approximately 9.6% and the gas temperature reaches over 600°C.

Then, the gaseous mixture is cooled in the first boiler, generating medium-pressure steam and cooling to 410 – 420°C.

A four-beds catalytic reactor admits the gaseous flow and, as SO₂ is gradually converted into SO₃, a considerable amount of heat is generated due to the highly exothermal oxidizing reaction. The process is approximately 99.2% efficient.

Furthermore, the gas is cooled to 250 – 300°C, generating steam through a medium-pressure boiler before entering the absorption step. Its high SO₃ content is greatly reduced in the absorption tower, in which sulfuric acid is generated and increases in concentration through the exothermic reaction of SO₃ and water. The acid current reaches the bottom of the tower at approximately 120°C and is directed towards a circulation tank, in which it is diluted with water and reaches a concentration of 98.5%.

The acid leaves the circulation tank and is pumped to a heat exchanger, which reduces its temperature to 80°C with cooling water. Afterwards, it flows towards drying and absorption towers, in which SO₃ is absorbed.

Outlet effluent gases from the absorption tower are virtually contaminant-free, containing less than 50 mg/nm³ of SO₃ and 600 ppm of SO₂. In order to further reduce content of these substances, the absorption step a hydrogen peroxide scrubber is installed downstream, in which SO₂ content reaches below 400 volumetric ppm and produced diluted acid is utilised as process water primarily towards acid concentration control in circulation tanks. Overall, the acid plant designed for this facility generates:

- 150 000 tpd of sulfuric acid at 98.5% concentration.
- Dried air with less than 400 volumetric ppm of SO₂.
- 4 tph of medium pressure steam.

Conclusion

Modular acid plants are a cost and production-effective solution for companies reliant on sulfuric acid either as raw material or productive asset. Industrial facilities that incorporate such technology are able to count on several benefits from on-demand production of acid and steam, mitigation of atmospheric production and enhanced, non-dangerous energetic integration provided by the company's heat recovery system. **WF**

References

1. CLARK, N., et al., 'Do Small, Modular Acid Plants Fit in a World of Mega Plants?', Sulfuric Acid Today (2017), p. 20.
2. CLARK, N., et al., 'Safely Increasing Energy Generation', SULFUR (2017), pp. 3 – 7.

Table 1. Results comparison of corrosion through a leak hole.

Fluid pair	Conditions	Results
Water 98% sulfuric acid	2 mm hole Started at ambient temperature Peak temperature 66°C 316 L stainless steel	Corrosion rate: >145 mm/year
CS270 inert fluid 98% sulfuric acid	2 mm hole 72 hr test duration Started at ambient temperature 316 L stainless steel	Corrosion rate: 0 Mass lost: 0

