

Number 373

November | December 2017

# SULPHUR

[www.sulphurmagazine.com](http://www.sulphurmagazine.com)

**Heat recovery in acid plants**





**Kalium Mineração**  
First SAFEHR® plant

---

Clark Solutions SAFEHR® is a patented sulfuric acid heat recovery technology that addresses issues such as safety and corrosion in an absolutely innovative way.

SAFEHR® technology can increase high pressure steam generation in an acid plant by almost 20% and total energy recovery by as much as 35%.

SAFEHR® is a registered trade mark of Clark Solutions.

# Safely increasing energy generation

Clark Solutions' SAFEHR® heat recovery technology is a new approach to sulphuric acid production which addresses issues and concerns with regard to corrosion, shutdown and hydrogen explosions to make heat recovery safer than conventional operation. **Nelson Clark** describes the SAFEHR® technology, benefits and uses to help the acid plant operator recover energy efficiently and safely.

**S**ulphuric acid plants are energy producers. Sulphur burning and spent acid recovery plants burn sulphur or fuel to produce SO<sub>2</sub> gases while generating heat. The reaction of oxidation of SO<sub>2</sub> into SO<sub>3</sub> is also exothermic and produces heat. Finally, both moisture and SO<sub>3</sub> absorption into the strong acid generates heat along towers packings.

The major exothermic reactions on which heat is generated in a typical plant are:

Sulphur combustion:  $S + O_2 \rightarrow SO_2$

SO<sub>2</sub> oxidation:  $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

SO<sub>3</sub> absorption:  $SO_3 + H_2O \rightarrow H_2SO_4$

In a typical sulphur burning plant heat is generated in many process units. Table 1 shows the heat generated at different stages in a typical 1,000 t/d plant, operating at 11.5% SO<sub>2</sub> concentration.

Standard heat recovery technology uses sources 1 to 5 to generate energy by typically producing superheated high pressure steam, up to 63 bar and 480°C. The energy from sources 6 to 8 is usually rejected to the atmosphere via cooling water towers.

Table 2 shows the heat recovery on a standard high efficiency sulphur burning plant.

The fraction of heat recovered is converted into high pressure steam which, in turn, is used to generate electrical power and/or used for other heating purposes such as phosphoric acid evaporation, etc.

This was the standard for heat recovery in sulphuric acid plants until the early 1980s. As a general rule, a very efficient double absorption sulphur burning acid

**Table 1: Heat generation in a 1,000 t/d 3+1 double absorption sulphur burning plant**

Source	Equipment	Generated heat (MW)	Temperature level (°C)
1	Sulphur furnace	33.8	1125
2	Catalytic bed 1	6.9	625
3	Catalytic bed 2	2.9	530
4	Catalytic bed 3	1.1	460
5	Catalytic bed 4	0.6	433
6	Drying tower	1.7	85
7	Interpass absorption tower	14.8	110
8	Final absorption tower	4.3	90
<b>Total heat generation</b>		<b>66.1</b>	

Source: Clark Solutions

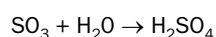
**Table 2: Heat recovery on a standard, high efficiency, sulphur burning plant**

Sources	Equipment	Recovered heat (MW)	Temperature level (°C)
1, 2	Waste heat boiler	33.8	425
2, 3	Superheater	6.9	440
3, 4	Economiser	2.9	180
4, 5	Economiser	1.1	160
<b>Total heat generation</b>		<b>45.3</b>	

Source: Clark Solutions

plant would recover no more than 65% of the total heat generated at the plant.

With the advent of heat recovery processes to recover heat from the interpass absorption step from the reaction

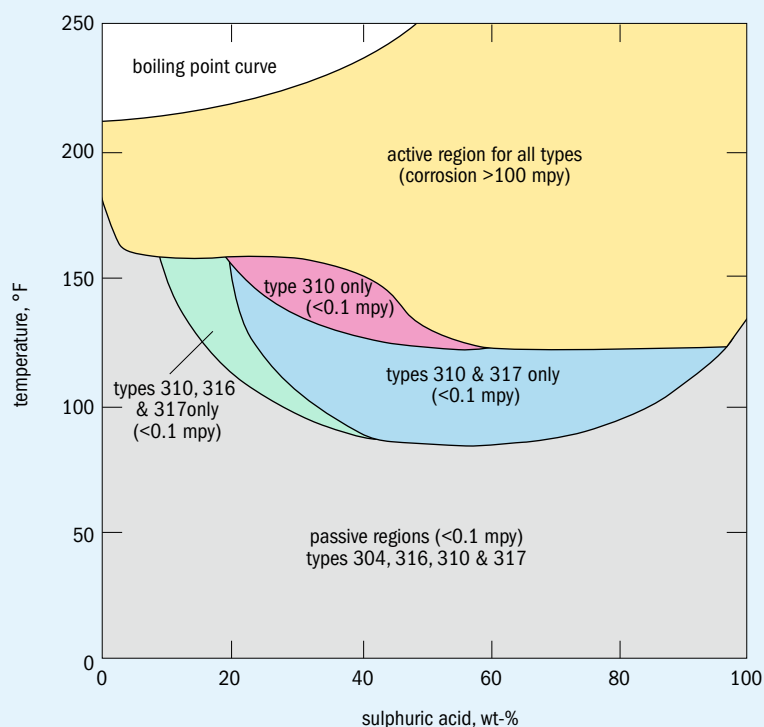


the total heat recovery from sulphuric acid plants rose from 65% to 90%.

The success and quick investment recovery obtained with heat recovery at the interpass towers has on a few occasions been followed by corrosion, shutdown and explosion concerns.

In the few cases where boiling water leaked into the strong hot acid, the effect was very harmful for the operation. The water-acid reaction at high temperatures

Fig. 1: Isocorrosion curve for sulphuric acid



is very exothermic and very quick; as the reaction takes place acid dilutes and heats up and, particularly at the leak location, gets more corrosive, accelerating the corrosion process.

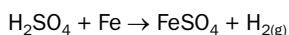
The failure of the heat recovery boiler can be catastrophic; in addition to the failure itself, as a general rule, the acid plant and consequently the entire complex is required to shut down, making failure costs escalate.

Sometimes, downtime is much more critical than the costs of damaged equipment; some plants, to avoid the unexpected shutdown, have built tower independent heat recovery towers and heat recovery systems to protect against such a failure.

The failure of a boiler or of the acid cooler is still a critical problem that can potentially shut the plant down in case of hydrogen explosions.

## The hydrogen generation issue

Corrosion of iron by sulphuric acid generates hydrogen according to the following:



The rate of hydrogen formation increases alongside acid operating temperatures.

Hydrogen can damage equipment by several mechanisms, such as solid solution

hardening and hydrogen embrittlement, blistering and others. It can also accumulate at high points in the plant and ignite, causing explosions.

The recent literature registers several hydrogen explosion events, in the five continents. All of them were followed by enormous damage to equipment, property and in some cases people.

In normal operation, within the standard <1 mil/year corrosion rates, the generation of hydrogen is minimal (see Fig. 1). As strong acid dilutes, its corrosiveness increases and hydrogen generation rises accordingly.

So, in order to definitively avoid hydrogen formation and its deleterious consequences, while not losing the benefits of heat recovery, it is important to avoid the formation of weak acid.

With this concept in mind, Clark Solutions has developed and patented SAFEHR® Heat Recovery Technology.

## The SAFEHR® concept

The concept behind SAFEHR® technology is the use of a family of proprietary inert fluids, CS fluids, to work as intermediate media between the hot acid and boiler feed water.

The CS fluid products present a series of properties that make them unique for working as intermediate media in such systems:

- Inert to acid and water: the fluid is totally inert to acid (in any concentrations) and water.
- Non-corrosive: they can be used with virtually any materials without any corrosion risk, being compatible with strong acids, water, organics fluids among others.
- Non-toxic: the fluid is FDA approved and its handling and storage requires no special measures.
- Non-flammable: it will not catch fire, even if an ignition source is put in contact with hot fluid.
- Non-oxidant: oxygen or atmospheric air will not oxidise the fluids, so they can be used and store in non-blanketed environments.
- High boiling points: boiling points will vary between 200°C and 300°C, depending on the fluid and application selected.
- Density in-between water and acid: fluid densities at operating temperatures will be between 1,3 g/cm³ and 1,5 g/cm³, in between that of liquid water, 880-980 g/cm³, and strong acid, 1,6 -1,8 g/cm³, keeping the phases separated even in leakage situations.
- Low vapour pressures: usually less than 20 mm w.c. what will minimise losses by evaporation.
- Odour: fluid is odourless and requires no mask or other respiratory devices while being handled.

Basically the SAFEHR® system is a closed loop, where hot acid is cooled by the CS fluid, which in turn heats the boiler feed water:

Fig. 2 shows the SAFEHR® closed loop for high temperature conditions.

The CS fluid is a polymeric fluid, inert and immiscible to both water and sulphuric acid.

The CS fluid system is maintained at a pressure below the acid and water systems so in the event of a leak, the leaking fluid follows into the CS fluid circuit, which will allow the leak to be identified.

The interfacial tension and density differences between the fluids make a liquid liquid coalescer an excellent storage tank. Acid will settle at the bottom of the coalescer and water will stay at its top, so, even in the improbable case that both fluids would leak, there would still be no

contact between them. The coalescer/settling tank is designed to easily segregate the fluids. Conductivity and level control guarantee that a leak is quickly identified.

Fig. 3 shows corrosion promoted by sulphuric acid with water contact (left) and CS 270 fluid contact (right).

## SAFEHR® applications

Hydrogen explosions are not limited to conventional heat recovery plants. In Brasil, in the last ten years, three acid plants have registered hydrogen explosions. Two of these were acid cooler leak related. None of them produced personnel injuries but all of them caused major equipment and loss of production costs.

## Conventional plants

SAFEHR® as a concept can be used in existing plants, as an intermediate cycle in the acid cooling circuit (see Fig. 4).

In this case, the strong acid system will be protected from leaks, even in upset conditions.

The strong acid cooler can be either a shell-and-tube unit or a plate unit; this last one will require smaller coolant fluid loads. The water heater will be a plate unit built in 304/316 stainless steel as there is no corrosion risk on this side of the process.

The water side of the strong acid cooler will be protected and free from corrosion or incrustation as it will be only in contact with the CS fluid, inert and thermally stable. In such a case, the purpose of SAFEHR® is to add reliability to the acid cooling system(s) and eliminate the hydrogen explosion risk.

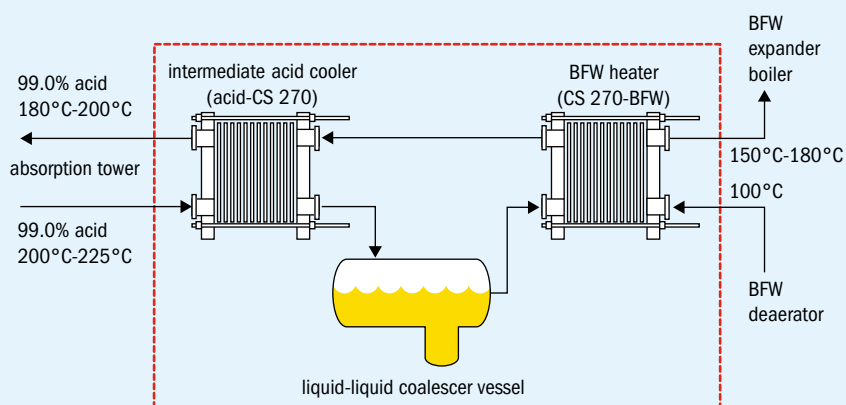
## Existing heat recovery systems

An existing heat recovery system can benefit from a skid mounted SAFEHR® system as a replacement to the strong acid to boiler feed water exchanger.

This will aggregate safety to the process and allow for the boiler to be constructed of less expensive materials.

While a boiler feed water leak will flow to the acid system in a conventional system, requiring the shut-down of the whole acid plant or the heat recovery unit, in a SAFEHR® unit the leak will flow into the SAFEHR® skid, with no contact between fluids, allowing the operator to plan the maintenance in advance.

Fig. 2: SAFEHR® closed loop for high temperature conditions



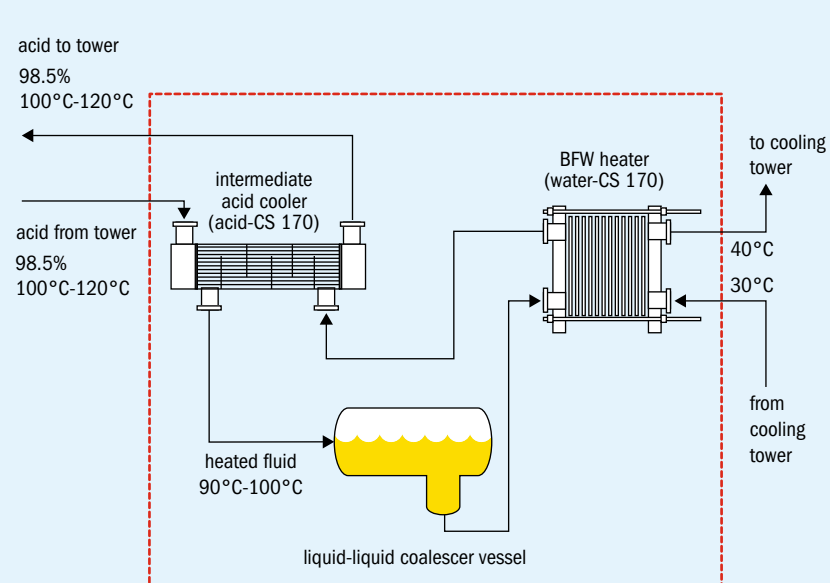
Source: Clark Solutions

Fig. 3: Corrosion promoted by  $H_2SO_4$  with (L) water and (R) CS 270 fluid contact



PHOTO: CLARK SOLUTIONS

Fig. 4: SAFEHR® closed loop for conventional operating conditions



Source: Clark Solutions

Fig. 5: SAFEHR® schematic

Source: Clark Solutions

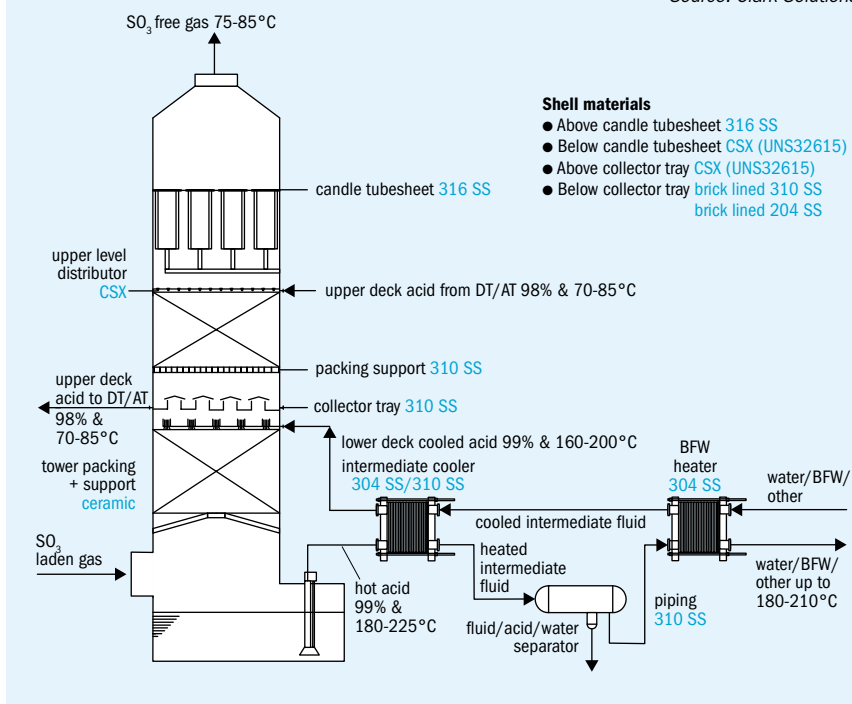
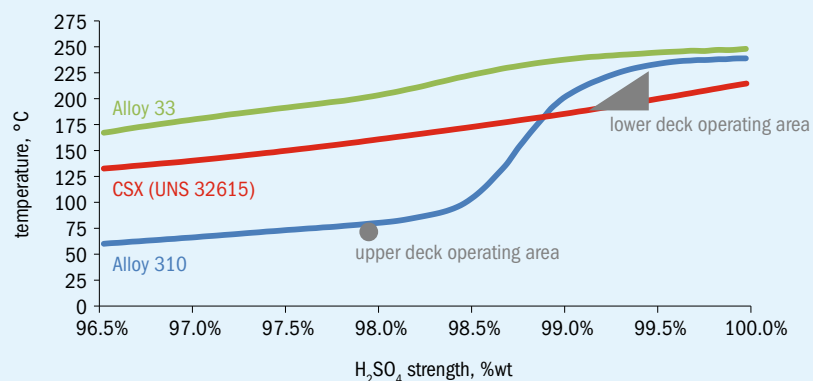


Fig. 6: SAFEHR® operating envelope



Source: Clark Solutions

## Complete system

SAFEHR® can also be implemented as a complete system (see Fig. 5). In this case Clark Solutions chose to design the system using 99.0-99.5% sulphuric acid as an absorbing media as this will allow the use of less expensive 310S stainless steel materials. Nothing, however, prevents the system from being built for 98.0-98.5% acid and using Alloy 33 or CSX stainless steel (UNS32615).

The complete system is basically composed of a two-stage absorbing tower with integrated pump booth, an acid pump and the SAFEHR® system.

The SO<sub>3</sub> admitted to the bottom of the tower is absorbed in the lower packing deck, where the reaction heats the acid to 220-225°C. The gases leaving this stage pass through a collector tray where they get remixed before it reaches the upper packing deck.

The hot concentrated acid from the bottom of the tower is pumped from the pump booth by a vertical centrifugal pump into the intermediate cooler where it exchanges heat with the CS fluid. The fluid is circulating in an enclosed system and heats boiler feed water or other fluids in this circuit.

The collector tray brings a substantial benefit to the energy recovery as it avoids

cool acid mixing with the bottom section acid, cooling it down and reducing the bottom temperature.

At the top of the upper deck, cold acid is irrigated in order to condense mist and absorb any non-absorbed SO<sub>3</sub> traces from the lower deck. This guarantees maximum absorption and minimal acid mist carryover.

Once the upper level acid, from the drying tower or the final tower depending on plant arrangement, reaches the top of the collector tray, it is collected and re-routed by gravity back to the tower from which it came.

The upper deck as well as the piping system to it, can be designed for full absorption of SO<sub>3</sub>, allowing the tower to operate with or without the intermediate loop.

The gases, free of SO<sub>3</sub>, flow through candle mist eliminators where the fine acid mist is captured and the gas flows to the process or to the stack/scrubber in single absorption systems.

## The intermediate cooling system

The intermediate cooling system can be supplied as separate skid for an existing plant or as part of a new heat recovery system.

It is composed of an acid-fluid heat exchanger, a liquid-liquid coalescer, pump, fluid-water heat exchanger and a buffer vessel.

The acid-fluid heat exchanger can be a plate exchanger, a shell-and-tube exchanger or an Alfa-Laval Compabloc fully welded exchanger. The choice of exchanger depends on the acid temperature and water pressure levels in the system.

The pressures are controlled so that the fluid circuit operates at the lowest pressure condition. In the case of eventual leaks, the pressure difference forces liquids into the intermediate loop. Acid leaks will reach the coalescer, while water leaks will circulate to the buffer or coalescer vessel. Acid leaks will be detected at the bottom of the coalescer by conductivity while water leaks will be indicated by a liquid level increase in the system.

Acid leaks will not accelerate as there is no heat of dilution or weak acid formed at the leak area, thereby conditioning the localised corrosion process to evolve slowly, giving time for a planned shutdown.

## Materials of construction

SAFEHR® is designed to be safe and last for many decades. Materials of construction are chosen accordingly. Fig. 6 shows the SAFEHR® operating envelope.

Fig. 7: Steam system schematic

Source: Clark Solutions

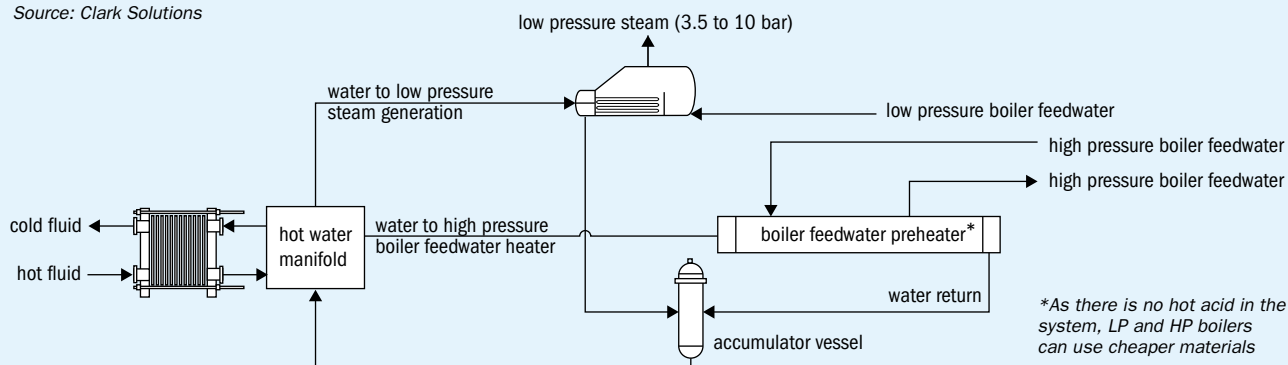
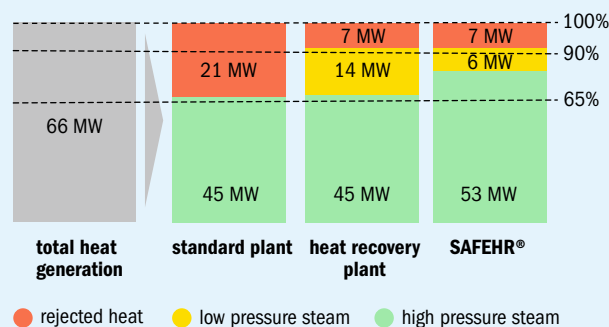


Fig. 8: Heat recovery comparison chart



Source: Clark Solutions

Table 4: Steam production on a 1,000 t/d plant with several energy options

	No heat recovery	Heat recovery	SAFEHR®
High pressure steam, t/h	54.0	54.0	65.2
(40 bar and 400°C), MW	44.4	44.4	53.6
t/t	1.3	1.3	1.56
Low pressure steam, t/h		20.8	7.6
(10 bar saturated), MW		14.6	5.4
t/t		0.5	0.18

Source: Clark Solutions

The SAFEHR® tower is built of three different material sections.

The bottom section and the pump booth, where the hot strong acid is stored, is brick lined 310S. The 310S stainless itself is extremely resistant to the operating conditions, but, the extra care with brick lining will guarantee the long term reliability and reduce risk of hydrogen generation and presence of nickel and chromium in product acid.

The collection tray is a 310S stainless construction.

From the collection tray and above, up to the candles tube sheet, the construction is SX®. In this region, acid at 80°C will pose no risk to SX. This section could be built using 310S stainless, but as Fig. 6 shows, the operation would approach the 1 mil/year line and per design principle Clark Solutions chose to keep corrosion below that limit whenever possible.

Tube sheet, candles housing and outlet duct are built of 316L stainless steel.

Entering the intermediate system, the acid fluid exchanger is a 310S construction (Compabloc) or 310S (tubes and headers) and 304S (shell) in the shell-and-tube case.

The fluid-water heat exchanger can be carbon steel/304/316, plate, spiral or shell and tube exchanger, depending on how heat will be distributed. Important to notice however is that the SAFEHR® boiler can be made of less expensive materials as it will be handling water instead of sulphuric acid.

The liquid-liquid coalescer is a cylindrical, vertical, 3 phase vessel equipped with a 316/310S plate-pack coalescer to keep phases (water/acid/fluid) separated even in the case of a leak.

The main acid pump is CD4MCu while the intermediate circuit fluid pump is a 316 SS centrifugal pump as well as the piping and expansion tank.

## Steam system

With SAFEHR® there are no limits as to how to use the recovered heat. For instance, part of the energy could be used to heat high pressure boiler feed water as shown in Fig. 7.

As an example, an acid plant that produces 1,000 t/d without a heat recovery

system would produce approximately 54 t/h of 40 bar and 400°C steam.

If it had a conventional heat recovery system, an additional 20 t/h of saturated 10 bar steam could be produced.

With SAFEHR® some of the energy used to produce low pressure steam could actually be shifted into high pressure. For example, if all the available heat could be used to pre-heat boiler feed water at 40 bar from 60°C to 180°C there would be an increase of 20% in the amount of high pressure (see Table 4 and Fig. 8).

SAFEHR® heat, in the form of hot water or steam can be used for other purposes.

## Conclusion

SAFEHR® is a new approach to the acid production. While adding a great deal of safety to the process and reducing corrosion risk, this is accomplished without any substantial energy losses. On the contrary, depending on the arrangement the SAFEHR® system it can improve quality of steam, a particularly interesting advantage for plants generating electrical energy. ■

# MORE THAN EQUIPMENT, **SOLUTIONS**

**Mist Eliminators:** MaxiMesh® and FiberBed®

**Tower Internals:** MaxiSaddle® and MaxiDome®

**Acid Distributors:** Through & Downcomers / Pipe Distributors.



**MIST ELIMINATORS**



**ACID DISTRIBUTORS**



**TOWER INTERNALS**

**USA**  
411 SE Mizner BLVD #72  
Boca Raton FL 33432-6001

**Brazil Office**  
281 Av. Moema  
Moema / SP 04077-020

**Embu Plant**  
91 Dn. Joaquina - Moinho Velho  
Embu das Artes / SP 06807-690

**Chile Plant**  
Volcan Lascar 801,2H  
Pudahuel - Santiago - Chile

