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Thermal and Mechanical Separation Solutions

SAFELY INCREASING ENERGY GENERATION
SAFEHR

SAFEHR®

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 describes the SAFEHR® technology, benefits and uses to helps the acid plant operator recover energy efficiently and safely.

Sulphuric acid plants are energy producers, Sulphur burning and spent acid recovery plants burn Sulphur or fuel to produce SO_2 gases while generating heat.

The reaction of oxidation of SO_2 into SO_3 is also exothermic and produces heat. Finally both moisture and SO_3 absorption into the strong acid generates heat along towers packings.

In a typical Sulphur burning plat 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_2 concentration.

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

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

Sulphur Combustion

- $S + O_2 \rightarrow SO_2$
- SO_2 Oxidation: $SO_2 + ½\, O_2 \rightarrow SO3$
- SO_3 absorption: $SO_3 + H_2O \rightarrow S_2SO_4$

Table 2 shows the heat recovery on a standard high efficiency Sulphur burning plant:

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
	Total heat generation	66.1	

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
	Total heat generation	45.3	

Source: Clark Solutions

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

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

$$SO_3 + H_2O \rightarrow H_2SO_4$$

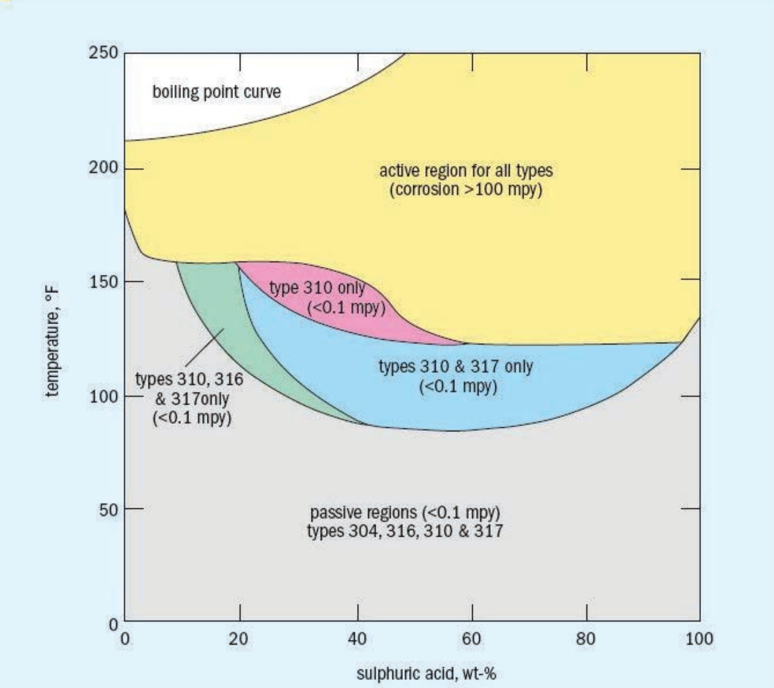
The total heat recovery from sulphuric acid plants rose from 65% to 90%.

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

In the few cases boiling water leaked into the strong hot acid, the effect was very harmful for the operation.

The water-acid reaction at high temperatures 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.

Fig. 1: Isocorrosion curve for sulphuric acid



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, downtimes is much more critical tha the costs of damaged equipment, some plants, to avoid the unexpected shutdown, have built tower independente heat recovery towers and heat recovery systems to protect against such a failure.

The failure of a boiler oro f 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:

$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_{2(g)}$$

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 continentes.

All of them were followed by enormous damage to equipment, property and in some cases people.

In normal operations, 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 acid 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 proprieties 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 with not catch fire, even if an ignition source is put in contact with hot fluid.
- 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/cm^3 and 1,5 g/cm^3, in between that of liquid water, 880-980 g/cm^3, and Strong acid, 1,6 -1,8 g/cm^3, keeping the phases separated even in leakage situations.
- Low vapour pressures: usually less than 20 mm w.c. what will minimize losses by evaporation.
- Odour: fluid is odorless and requires no mask or other respiratory devices while being handled.

Basically the SAFEHR® systems 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 fuid is a polymeric fluid, inert and immiscible to both water and suphuric acid.

The CS fluid systems 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.

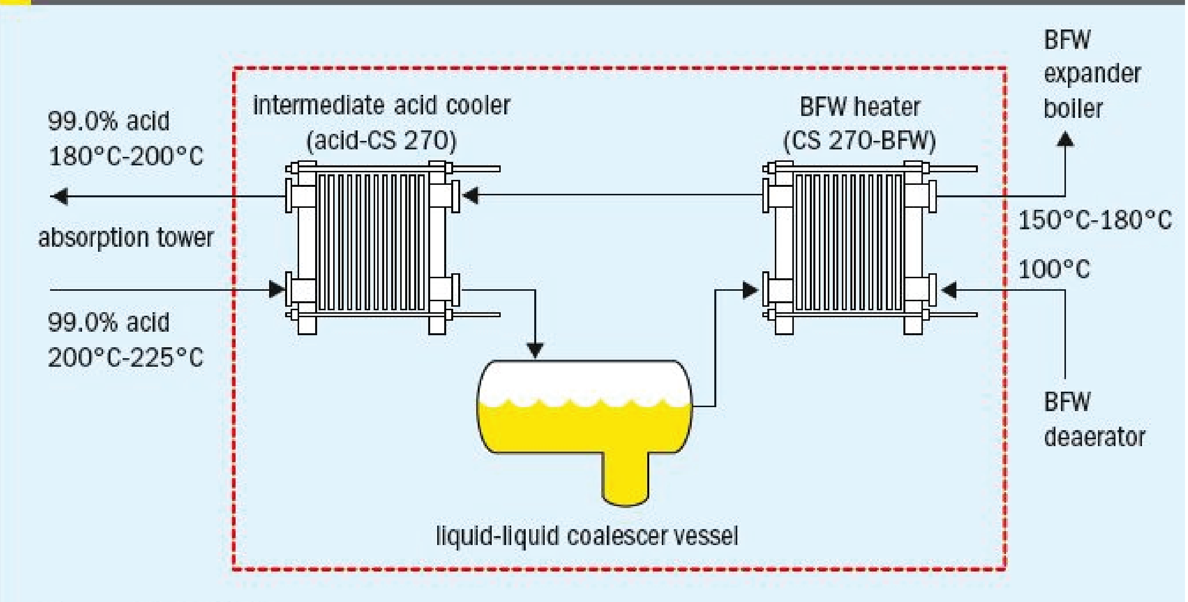
The interfacial tension and density differences between the fluids make a liquid liquid coalescer in a excellent storage tank.

Acid will settle at the bottom of the coalescer and water will stay a tis 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 shoes corrosion promoted by sulphuric acid with water contact (left) and CS 270 fluid contact (right).

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



Source: Clark Solutions

SAFEHR® Applications

Hydrogen explosions are not limited to conventional heat recovery plants. In Brazil, 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.

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

Conventional plants

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

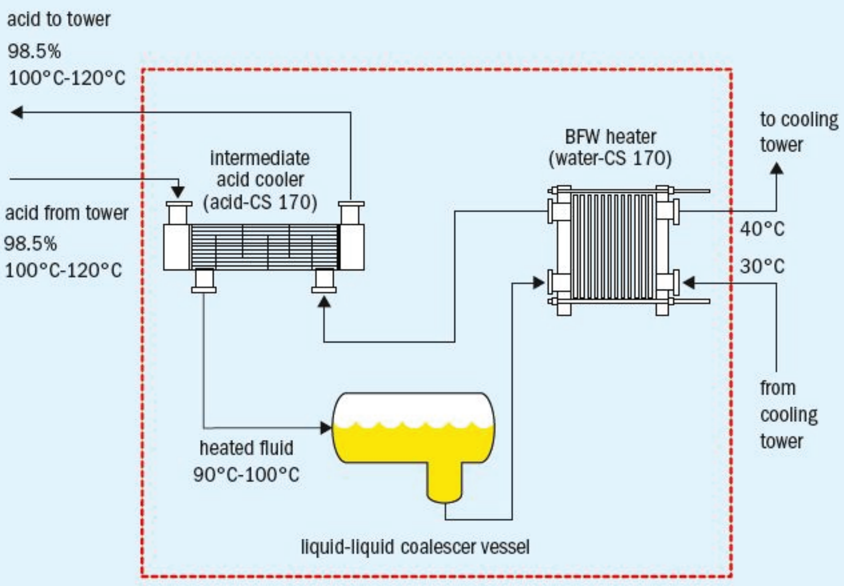
In these cases, the strong acid system will be protected from leaks, even in upset conditions. The strong acid cooler can be either a shell-and-tube unit or a plate unit; this last one will requires smaller coolant fluid loads.

The water heater will be a plate unit build in 304/3016 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 form corrosion or incrustation as it will be only contact with the CS fluid, inert and thermally stable.

In such case, the purpose of SAFEHR® is to add reliability to the acid cooling system(s) and eliminate the hydrogen explosion risk.

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



Source: Clark Solutions

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

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% suphuric 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 SO3 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 mixing with the bottom section acid, cooling it down and reducing the bottom temperature.

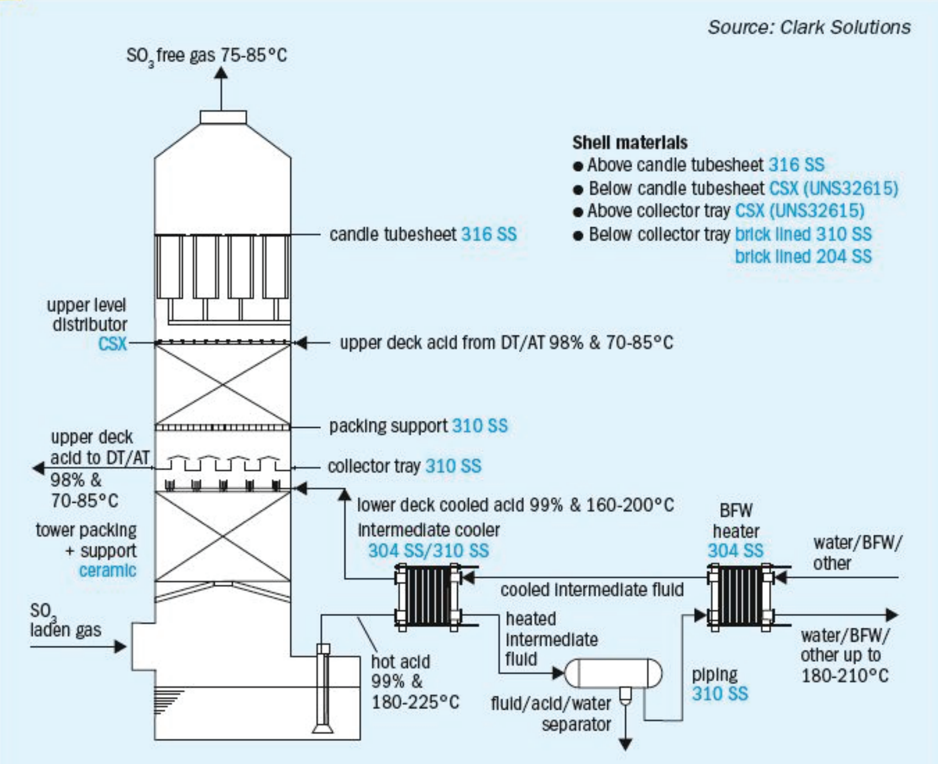
At the top of the upper deck, cold acid is irrigated in order to condense mist and absord any non-absorbed SO3 traces from the lower deck. This guarantees maximum absorption and minimal acid mist carryover.

Once the upper level acid, from the drying tower or the final tower depending on plant arrangement, reaches the top off 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 SO3, allowing the tower to operate with or without the intermediate loop.

The gases, free of SO3, flow through candle mist eliminators where the fine acid mists captured and the gas flows to the process or to the stack/scrubber in single absorption systems.

Fig. 5: **SAFEHR® schematic**



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 pressures difference forces liquids into the intermediate loop.

Acid leaks will reach the coalescer, while water leaks will circulate to the buffer or coalester 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 ow weak acid formed at the leak area, thereby conditioning the localized corrosion process to involve slowly, giving time for a planned shutdown.

Materials of construction

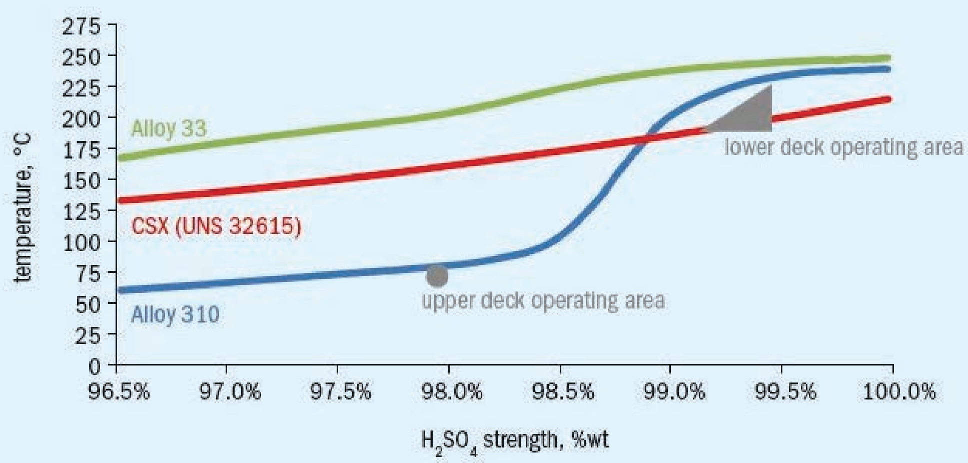
SAFEHR® is designed to be safe and last for many decades. Materials of construction are chosen accordingly. Fig.6 shows the SAFEHR® operating envelope.

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.

Fig. 6: **SAFEHR® operating envelope**



Source: Clark Solutions

From the collection tray and above, up to the candles tube sheet, the construction is SX®. In this region, acid at 80C will pose no risk to SX.

This section could be built using 310S stainless, but as Fig. 6 shows, the operation would approach the 1mil/year line and per design principle Clark Solutions chose to keep corrosion bellow that limit whenever possible.

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

Entering the intermediate system, the acid fluid exchangers is a 310S construction (Compabloc) or 310S (tuber 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 phases vessel equipped with a 316/310S plate-pack coalescer to keep phases (water/acid/fluid) separated even in the cases of a leak.

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

Fig. 7: Steam system schematic

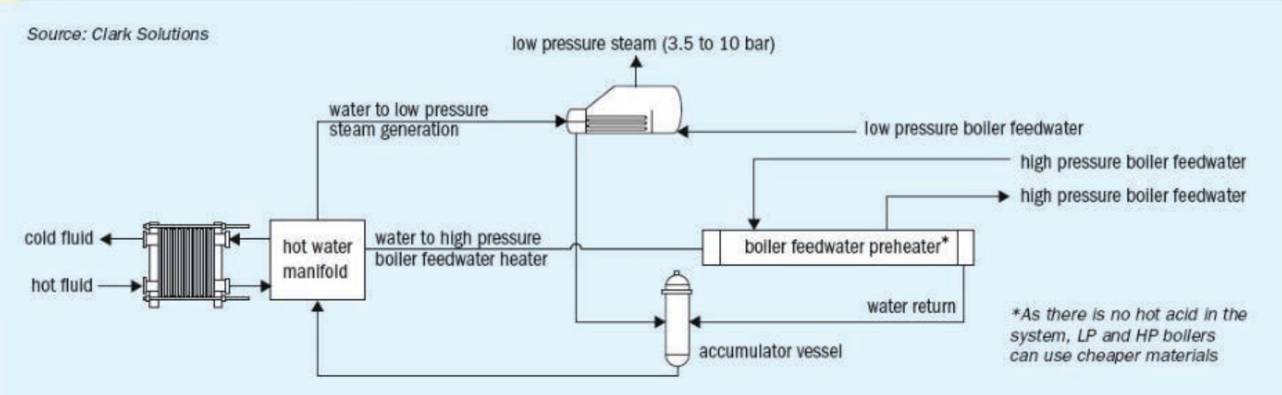
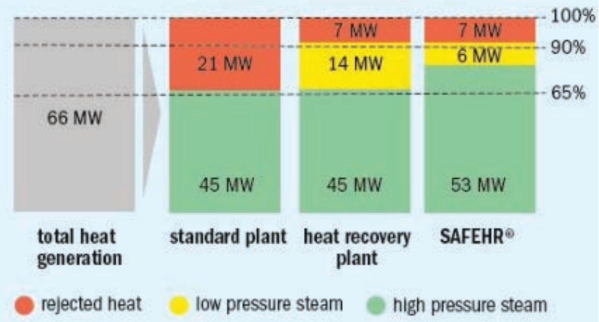


Fig. 8: Heat recovery comparison chart



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

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 400C steam.

It if had a conventional heat recovery system, an additional 20t/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.

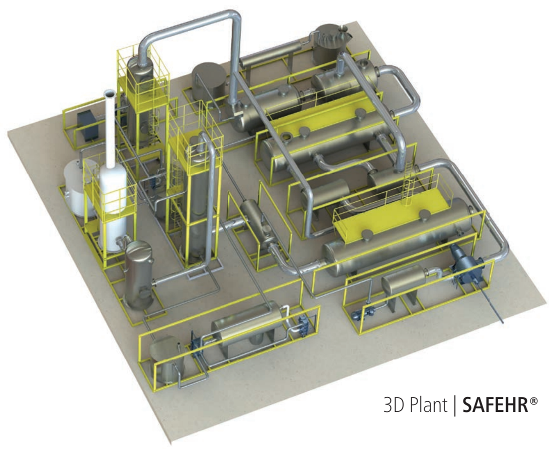
For example, if all the available heat could be an increase of 20% in the amount of high pressure (see table 4 and Fig.8)

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 corrosions 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.



3D Plant | **SAFEHR®**