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Process Heat Recovery and Digitalisation in Sulphuric Acid Plants

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Abstract

Energy efficient processes with maximised heat recovery and efficient operation have moved more and more into focus in the sulphuric acid business. Even metallurgical plants are now expected to produce high pressure steam for power generation. With the help of proven processes, like the Outotec LUREC™, HEROS™ and HIPROSTM technologies this demand can easily be satisfied. Heat recovery causes interconnections between different areas of a complex to become more common. Additionally, individual plants have increased in complexity, which both leads to higher requirements for operational personnel. The unfortunate combination of higher personnel mobility and fluctuation with remote locations of green or brown field sulphuric acid plant projects results in often less experienced personnel, who need support to operate today’s state of the art sulphuric acid plant. By combining Outotec’s process knowledge with actual operational data of the plant, a digitalisation system can greatly assist operation. The combination of higher efficiency and assistance through digitalisation will be further detailed in the Outotec presentation.

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1. Nature of Heat Recovery

Due to the exothermal reactions taking place in a sulphuric acid plant, the recovery of process heat generated in the oxidation sections (sulphur furnace / converter section) is commonly known. Also the recovery of process heat generated at the drying- and absorption section of a sulphuric acid plant goes back to the late 1970ies and 1980ies. Outotec implemented heat recovery in Europe first, mainly in Scandinavia. Hot water was produced and fed into

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municipal district heating systems. The technology is still in use today, also when new plants are built in this region. Obviously, this technique is not applicable in milder climates.

Later, the hot water was produced and used for sea-water desalination at a multiple stage evaporation plant. In 2003, Outotec has also built a phosphoric acid concentrator, being fed with hot water instead of the traditional low pressure steam.

Obviously, the most interesting use of the said energy is for generation of steam, either for process purposes or for electricity generation. The first installations go back to the 1990ies and one of the first Outotec designed heat recovery plants (120 metric tpd H₂SO₄ (Mh)) was in operation for more than 25 years, producing 5 bar saturated steam. Earlier this year Outotec has replaced this installation by a more efficient and modern technology. Please see below a typical distribution of energy in a sulphuric acid plant at the following Sankey diagram, Figure 1.

![Sankey Diagram](image)

Figure 1: Sankey Diagram

A number of individual process steps are required to make commercial grade sulphuric acid from either elemental sulphur or SO₂ bearing off-gas from metallurgical operations, e.g. copper smelting. Those steps are typically the oxidation of sulphur to SO₂ through combustion, the catalytic oxidation of SO₂ to SO₃ in the converter section and the hydration of SO₃ with water H₂O to H₂SO₄. All of these steps are exothermic reactions, i.e. characterised by large amounts of excess energy or heat.

To enable a sulphuric acid plant to operate commercially beneficial, the recovery of said excess thermal energy and its transfer to useful electrical energy is desirable. Obviously, the higher the degree of recovery, the more beneficial is the process.

While sulphur oxidation and SO₂ oxidation occur at rather high temperatures, e.g. typically 390...630°C for the catalytic reaction, respectively 900...1,600°C for sulphur combustion, it is common to transfer said excess energy into high pressure steam (HP-steam). Conventionally, the hydration occurs at much lower temperature level, e.g. typically 50...120°C. Thus, thermodynamically the energy recovery in form of steam is not feasible. Traditionally, this energy is transferred to cooling water and wasted. The diagram Figure 1, presents the relative approximate amounts /
distribution of energy at a sulphur based acid plant.

Traditionally, about 60% of the initial energy is potentially recovered in form of HP-steam, while a large amount of the energy, - the remainder of almost 40%, is related to acid cooling and eventually dissipated to the environment, typically via evaporative cooling.

In order to transfer a significant part of the said 40% portion to useful energy, the production of low pressure steam (LP-steam) is an attractive option. LP-steam can be used for numerous process applications in the chemical industry, e.g. concentration of weak phosphoric acid, crystallisation of fertiliser or electricity generation. The latter is obviously most attractive, as electricity can be used as “by-product” of sulphuric acid making at virtually every location.

The overall degree of recovery increased gradually during the last years to typically ca. 90%. While others with heat recovery systems have targeted the maximisation of LP-steam, the Outotec HIPROSTM focuses on the maximisation of HP-steam. HIPROSTM can transfer part of the LP-steam to HP-steam and hence produce more electrical energy via the larger portion of the more valuable HP-steam. It appears, that Outotec’s currently achieved degree of energy recovery around the approx. 95% margin does not justify being subject to any further augmentation, simply by not being cost effective.

Designing a heat recovery system must observe certain criteria and priorities, which cannot be compromised:

1st Priority: Safety: The sulphuric acid plant has to be designed that operational issues are early detected and the plant can easily be brought into safe conditions; contributing factors are instrumentation, materials of construction, etc.

2nd Priority: Sustainable acid production is mandatory, as this is basically the rational for the sulphuric acid plant. Ensure that acid production is operative, irrespective of the heat recovery system being in operation or not. Impact on the acid production capability of the plant through failure or shut-down of the heat recovery system cannot be tolerated!

3rd Priority: Generation of low pressure steam does significantly improve the economics of the acid plant operation (essentially replacing fuel), but must not introduce obstacles and risks which may be in the way to ensure the commitment to priority 1.

4th Priority: Maximised high pressure steam production enables the acid making process at all, but also provides the basic economics for the plant through generation of electricity.

One major issue of any heat recovery process for LP-steam production is the need to operate part of the absorption section with concentrated sulphuric acid of very high temperatures, typically 200 to 220 °C. This is thermodynamically required when producing saturated LP-steam of e.g. 10 bar (a). Concentrated acid at approx. 200°C can be extremely corrosive unless a very strictly defined window of operation is adhered to, with respect to acid concentration and temperature. A few suitable materials of construction have been identified (stainless steel materials), but all are characterised by said window of operation, different in size for different materials.

The worst for an acid plant operation is that the plant must shut down and cannot continue operation when the heat recovery system is off line. The effect can be dramatic, as the unavailability of the sulphuric acid will seriously affect the downstream production units, e.g. phosphate digestion for P2O5-production or, in case of a metallurgical operation, shut down the upstream unit, e.g. copper smelter. So, the security of plant availability and the safety for plant and operators has been identified as a major concern.

2. The Technology of Heat Recovery in the Strong Acid Section

Though depending on local conditions, the economics are clearly in favour of the installation of a heat recovery system. The cost is moderate and the pay-back time is attractive. Obviously it requires a continuous demand for LP-steam in case this is used for process purposes. Otherwise, it is desirable to also feed this LP-steam into a turbine generator and produce electrical energy. The configuration and concept depends on local project circumstances. A principle flow-sheet of the Outotec HEROSTM technology is presented in Fig. 2.
Sulphuric acid of around 200°C can be very corrosive in case the correct concentration is not maintained, e.g. with a tiny leakage of water to the acid. Note, that the water (steam) pressure is higher than the acid pressure. Thus, any leakage will predominantly push water to the acid side. Such leakage is extremely difficult to detect or determine. At conventional acid plants, the liquid pressures are such, that always acid penetrates into the water side, which can easily be monitored by e.g. pH or conductivity. This is not the case at heat recovery systems and hence the serious potential of catastrophic corrosion.

Figure 3 below illustrates the limitations of the parameters, acid concentration and temperature, for various materials. The better the corrosion resistance, the better is the material suited for this purpose. With increased corrosion resistance (or wider window) however, also the specific cost for the material increases.

Accepting this means that the design must ensure and provide measures that in such case, the damage can be adequately mitigated.

What is of utmost importance is the fact, that the sulphuric acid plant must not be shut down in case the heat recovery system is taken out of operation, deliberately or forced! The plant must be able to continue operation to produce sulphuric acid for the downstream process, e.g. phosphate rock digestion, including HP-steam production. In case of a metallurgical plant, the upstream metal production would not tolerate a shut-down of the sulphuric acid plant either. This is a fundamental demand, which the Outotec design incorporates fully.
Wherever possible, Outotec has aimed to use conventional materials, i.e. carbon steel with brick lining. This material of construction is very well “forgiving” in case of accidently operating outside the concentration limit. Thus, the Venturi absorber, the intermediate absorber and the pump tank are all following the same design. The only stainless material which is exposed to the hot sulphuric acid is used for pumps, piping and the HEROSTM evaporator; there is no other choice. On top of this, we have chosen a material for these parts, which offers significantly higher corrosion resistance, and also a wider range of acid concentration before corrosion becomes a serious issue.

Outotec’s material of choice is the alloy Nicrofer 3033 (material number 1.4591), which offers a sustainable 0.1 mm/year corrosion rate at 200°C and 98.0 wt.-% H₂SO₄, respectively at 240°C and 99.7 wt.-% H₂SO₄ (see Figure 3). The material used by others in heat recovery systems is a specific type 310 stainless steel. It can tolerate a temperature of 200 °C only between 99.0 and 99.7 wt.-% H₂SO₄. On first sight this does not look to be a large difference, but in terms of corrosion it is a different world. Outotec is using Nicrofer3033, this practically doubles the width of the tolerable window in terms of acid concentration.

Furthermore, the Outotec HEROSTM evaporator design is based on a forced circulation water system. Instead of a conventional “re-boiler” type, we use a much smaller shell & tube type vessel. The result being, that the amount of water in the system is much less and hence it is easier and faster to separate / drain the water from the system in case of a leakage, thus minimising the exposure time.

A sophisticated control technology is also part of the process, enabling early detection of leakages or mal-operation and thus mitigating the damage to equipment and risk for the personnel.

As mentioned earlier, the Outotec heat recovery system HEROSTM can be taken out of operation while the sulphuric acid plant continues normal production. Moreover, we have developed our technology so, that we can ensure a smooth transition between the HEROSTM operation and the conventional inter-absorber operation. This is a significant improvement during start-up of the sulphuric acid plant. One does first stabilise the operation in the conventional inter-absorber mode and then slowly “activate” the HEROSTM. This is also valid vice versa, i.e. facilitates a controlled plant shut-down. In fact, this partial or combined HEROSTM can be operated continuously over a wide load range, meaning that a portion of the plant capacity is using the HEROSTM, while the inter-absorber will simultaneously operate with the balance.

In summarising the above, we are convinced that in the future heat recovery systems will be an inseparable part of all new sulphuric acid plants based on elemental sulphur combustion. This is mainly driven by the good positive
economics of such system. However, operating companies must be more alert and made aware of the nature and risk of this application. Outotec has introduced an improved safe and robust concept which will enhance the acceptance and reliability of these systems.

The amount of low pressure steam generated per ton of acid produced, is a typical performance figure, which however must be taken cautiously, as there are a number of influencing facts which contribute to the steam production, basically being:

- The temperature of the SO$_3$-containing gas entering the heat recovery unit. It is obvious that with higher gas temperatures, the steam production increases.
- The moisture content of the gas / air entering the drying tower. Higher humidity of the air will significantly reduce the steam generation. This is based on larger cross-flow from inter-absorption to drying tower (and vice versa), which leads to a shift of heat (energy) from the heat recovery system to the drying system.

**Further Features of the Outotec Heat Recovery System HEROSTM**

Venturi type absorption units have been built for many decades and used with good success for Outotec’s HEROSTM technology. A further improved feature is the process water addition device (or diluter) and the acid distribution to the packed bed tower.

The second absorption stage of the heat recovery system is designed as a packed bed tower, suitable to be operated as heat recovery tower with very small acid feed, as well as to be operated as a conventional intermediate absorber in case the HEROSTM is out of operation. In that case, the irrigation rate must be increased by an order of magnitude.

The acid concentration entering the HEROSTM venturi absorber must be controlled carefully and process water addition is used to adjust this concentration. A specially developed water diluter has been developed for this purpose, which ensures appropriate mixing of the hot acid and colder water. It is mainly made of glassfiber-reinforced Teflon with downstream enameled mixing tube. The mixing quality has also been simulated by CFD.

The Outotec HEROSTM technology does not require insulation of the absorption towers and pump tank, as the brick-lining is somewhat limiting the heat loss and also the design is not sensitive to temperature. This is also a substantial cost saving.

To minimise the heat losses, all the rest of piping, evaporator, etc. is obviously insulated at both technologies.

**3. High Pressure Steam Production**

In addition to the conventional design set-up for high pressure steam production in sulphuric acid plants based on sulphur burning, Outotec’s HIPROSTM technology employs a process feature, which is common in other industries, e.g. the power plant operation. To improve the overall thermal efficiency, power plants have operated the boiler feed water deaerator with elevated pressures, e.g. 10 bars instead of the conventional 1.2 bar at sulphuric acid plants. Essentially, it is characterised by using lower quality steam (= lower pressure) to generate higher quality steam. We have adapted this process parameter to the sulphuric acid plant, irrespective of the installation of a heat recovery system.

Conventional sulphuric acid plants often suffer from corrosion at the cold end of economisers, where the feed water enters with ca. 104 °C. This is very close to the acid dew point and upset situations will cause acid condensation, corrosion and eventually leakage of boiler feed water into the system. In case the deaerator is operated with say 9 bar pressure, the feed water will enter the economiser with ca. 175 °C, which is well above the acid dew point of the process gas. Thus, the deaerator operation with higher pressure does not only lead to more HP-steam production, but also to safer operation of the boiler plant.

The aim of the HIPROSTM technology is, to operate the deaerator of the boiler plant with higher pressure and temperature in order to increase the HP-steam generation. Simultaneously, the gas inlet temperature to the inter-absorber / HEROSTM shall be as low as reasonably possible, thus also positively contributing to the HP-steam flow rate.
4. Sulphuric Acid Technology and Digitalisation

Today’s world is a digital world. This can hardly be denied; just looking at our daily surroundings will reveal a lot of digital items: with e.g. smart phones, smart homes or even smart grids, a lot of technical products were turned “smarter” through digital transformation. That is exactly where it is needed to be precise about the meaning of “Digitise” vs. “Digitalisation”: The aim is not only to convert analogue to digital signals (“digitise”) but to create value using digital content.

In many cases, this digital content is readily available, but not or only used to a minor extent. At times, it is also necessary to gain the content first, e.g. trough new, smart sensors which were not available some years ago.

The driving forces and benefits for digitalisation are the same as experienced in almost all areas of business today, among others, these are: Improved efficiency and productivity, predictive analytics capability for equipment failure prevention and improvements in environmental compliance.

There are many examples and cases which demonstrate how much value can be extracted from digital content created in the industry. Only a few examples shall be given here:

- **Process simulators**
  Simulations have been used already in the Sulphuric Acid Industry by Outotec to train operators or as clones of the real plant to test and optimise the process itself including equipment. Improvements in the control system can be achieved long before the plant has been started up. Benefits are a more efficient operation with less downtime.

- **Advanced control systems**
  Predictive control of processes can improve the overall efficiency by using an internal model of the process as well as historical data collected during operation of the plant.

- **Remote diagnostics and maintenance**
  Reliability improvements have been achieved through remote diagnostics with early warnings as well as reductions in maintenance costs by avoiding unplanned shut downs. Equipment monitoring is done for e.g. heat exchangers in the oil refining industry as they are prone to fouling leading to energy and production loss.

Another general trend, which can be observed not only in the Sulphuric Acid Industry, is leading to more sophisticated and complex technological solutions. This trend is mainly caused by the need for higher energy efficiency due to high energy costs. Please refer to above mentioned steam generation with Outotec HEROSTM and HIPROSTM technology in sulphur based acid plants, where the generation of electrical power is optimised by an integrated system of low pressure and high pressure steam (HIgh Pressure Heat RecOvery System, HIPROSTM, see figure 4).

5. Outotec PORS – Plant Operability, Reliability and Safety System

As described above, a heat recovery system is designed to operate within small operational windows; also other applications result in additional complex cross linkages between different areas of the chemical facility to allow for optimum energy recovery. Even if a plant is designed without process constraints, the remote area location often found for green field projects or existing plants limits the availability of skilled and experienced operational personnel. In addition, higher personnel mobility leads to higher fluctuation and less opportunity for an operator to specialize in sulphuric acid.

To help operating companies to overcome this difficult situation, Outotec has developed the PORS - system which can guide and support operators in their work and create awareness for potential operational problems.
Usually large amounts of data are collected and made available through existing measurements in the plant but not used well enough to stay clear of failures or unplanned shut downs. Through digitalisation – bringing value to the digital content by combining it with Outotec’s process know-how, it delivers additional information about the process, plant and individual equipment.

The system is designed to be a standalone solution based on Outotec’s proprietary ACT platform which will receive all required process parameters and measurements from the DCS and present the results through its own user interface. It can be included as a part of a new installation or retrofitted for existing plants, covering the whole process chain with all areas, as shown in Figure 4.

The following chapter will describe the way the Outotec PORS-system is working for a sub-system of the Absorption Area, the acid coolers:

6. Module Example: Acid cooler monitoring

Monitoring of the acid coolers is crucial for successful operation of sulphuric acid plants as failures in acid coolers most probably will happen during the lifetime of the plant. If the failure is detected in time and the right measures are taken, operation can be continued after a relatively short shut-down for tube plugging or other maintenance and repair procedures. However, if the failure is not detected in time, the range of damaged equipment can stretch from just a single cooler to several equipment going as far as leaving the plant in a state of damage, which will not allow operation for quite a long time.

Figure 5 shows a basic flow sheet of an acid cooler, with acid being cooled on the shell side in a counter current flow to cooling water on the tube side. The bases of this module are heat quantity calculations, performed for both sides of the heat exchanger. Together with process information received from the DCS, as e.g.

- Cooling water flow rate
- Cooling water inlet temperature
- Cooling water outlet temperature
- Acid flow rate
- Acid inlet temperature
- Acid outlet temperature

and by using Outotec’s chemical properties database which is included in the Outotec PORS system, transferred heat on the water as well as on the acid side will be computed. As expected, both heat quantities should be equal, as long as heat transfer is not disturbed by e.g. acid leaking into the water side.
Both results will be compared by a special algorithm taking into account measuring in-accuracies and other plant specific factors. During normal operation with a healthy cooler the comparison algorithm delivers equal values for both heat quantities and no alarm will be displayed. In case of a difference in the heat quantities, an alarm will be displayed with additional information on the affected equipment and which could be the possible reasons for the alarm. Figure 6 shows the comparison of both streams and possible outputs of the PORS user interface.

Figure 5 – Outotec PORS - Sub-System Acid cooler

Figure 6 – PORS - Sub-System Acid cooler – Heat quantity comparison
Other possibilities to detect a cooler leakage include the strict monitoring of the pH or conductivity of the water side, as these values will rapidly change if acid is allowed to mix with the water side. This very straightforward way of detection is supported by the Outotec PORS-System through a sophisticated trend monitoring system.

Figure 7 shows an example of the operating mode of this monitoring system. The cooling water pH trend observed for quick changes as well as for constant values, as both can represent a problem in the plant. If no or only very minor changes in the pH are measured, this can often be caused by a faulty pH – sensor. Without proper pH measurement, the risk of not detecting an acid leak is extremely high, therefore a warning will be displayed with the advice to check the affected pH-sensor. As anticipated, a steep drop or other anomalies will cause an alarm of the PORS-system as well, as this is a potential sign of an acid cooler leak with acid being allowed to travel to the cooling water side.

Besides comparing heat quantities and monitoring trends for detection of possible leaks, further monitoring of the acid cooler performance is incorporated in this module. The performance of a heat exchanger can deteriorate over time as a result of accumulation of deposits on heat transfer surfaces. The layer often created on the cooling water side, represents additional resistance to heat transfer and causes the rate of heat transfer to decrease. The heat quantity transferred can be calculated as a function of log mean temperature difference, the heat exchanger area and the heat transfer coefficient.
Based on this calculation, the actual heat transfer coefficient will be calculated and compared to historical values, which were stored by the system for different plant loads. If the exchanger efficiency drops below a pre-defined value, a warning will be displayed (see Figure 8) to enable planning of cooler maintenance during the next shut down.

7. Conclusion

Based on today’s industry requirements the plant and process complexity is increasing; as a consequence, materials are designed to operate closer to their limits – all that is often caused by economical viability. Steam and power generation therefore play larger roles than ever before, even in metallurgical acid plants, where ease of operation and absolute reliability were the main focal points for a long time. Power generation in sulphuric acid plants is the preferable process design for modern acid plants. The Outotec HEROSTM process is also perfectly suitable as add-on solution in existing sulphuric acid plants with the potential of additional OPEX savings. To be able to satisfy the energy production demands as well as minimising the operational risks it is important to aim for designs with sufficiently large operational windows. Additionally, operation should be supported by means of digitalisation: the introduced PORS-System can guide operators with less experience and create awareness for potential operational problems, leading to a safer and more reliable operation of the plant.