

RECOVERING THE PAST

Rocky C. Costello, R.C. Costello & Assoc. Inc., USA, explains the history and chemistry behind a sulfur recovery technology undergoing a revival.

Several decades ago, the Aquaclus® sulfur recovery unit, developed by Stauffer Chemical, was touted as the future of sulfur recovery technology. It could be used as a tail gas unit on a large Claus plant or as a standalone system for smaller sulfur recovery plants. The sulfur dioxide (SO₂) content was said to be less than



10 ppm in the stack and it produced a bright yellow, molten sulfur. There were startup problems that developed and were never fully resolved due to the purchase of Stauffer Chemical by Chesebrough Ponds and the shutdown of the plant.

The process has the following features:

- Uses no catalyst.
- Makes pure, bright sulfur.
- Turndown capacity greater than 20 to 1.
- Processes high carbon dioxide (CO₂) levels, with low hydrogen sulfide (H₂S) content.
- Easily started and shut down.
- Exports energy as steam in most cases.

- Low OPEX.
- Results in no toxic byproducts.
- Can produce less than 10 ppmv SO₂ in the stack.
- Highly automated (low labour cost).
- Inexpensive chemical use.

After the bench scale plant was deemed to be viable, an approximately 28 tpd sulfur recovery pilot plant was built in Queen City, Texas, US, in the 1980s. The plant was fed by a single sour gas well that contained 21% H₂S at 1000 psig from the Smackover sour gas formation. At the wellhead was a gas fired heater and continuous methanol injection was

provided to prevent the formation of clathrates. A three-phase separator collected sour water, a sour natural gasoline stream and sour gas at the plant. The sour gas moved forward to an amine unit. The amine unit circulating 35% diethanol amine (DEA) separated the H₂S from the sour gas. The sweet gas was sent to a triethylene glycol (TEG) dehydration unit and then injected into the local transmission line. The residual sulfur content of the sweet gas was <4 ppmv. The acid gas was fed into the Aquaclus unit.

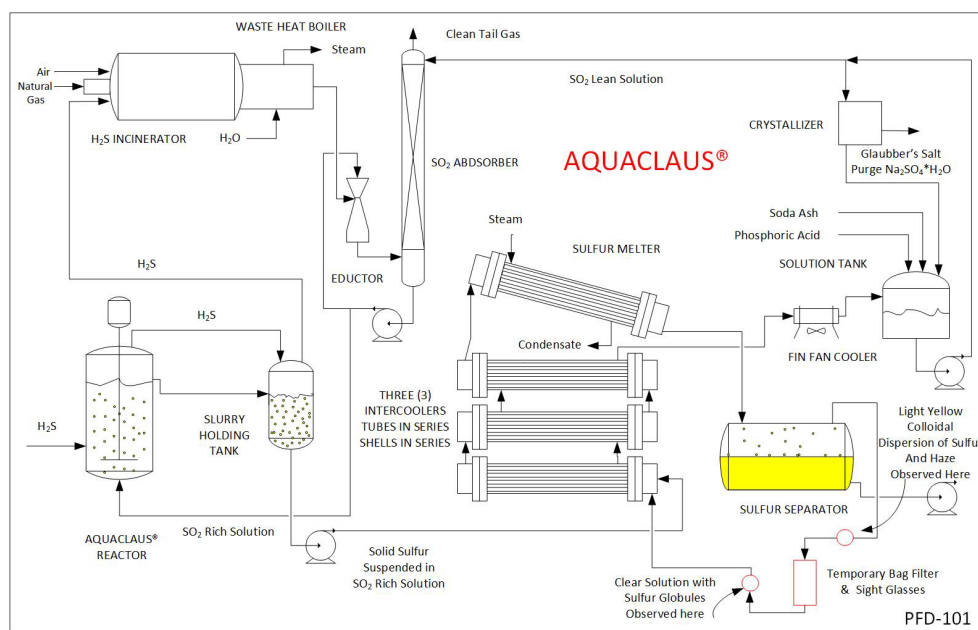


Figure 1. Flowsheet illustrating the original Aquaclus process.

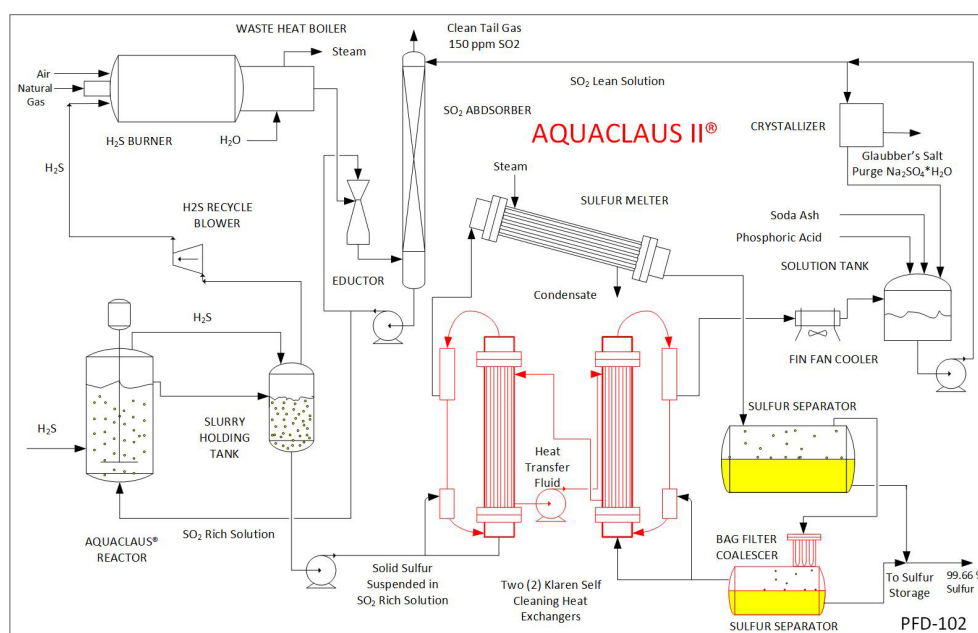


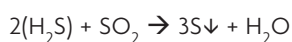
Figure 2. Flowsheet illustrating the Aquaclus II process.

Technology overview

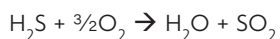
The circulating solution is produced from phosphoric acid, sodium carbonate and water. It can be thought of as somewhere between monosodium phosphate and disodium phosphate in composition. The solution effectively absorbs SO₂: the unit achieves less than 10 ppmv SO₂ in the stack gas. A byproduct stream of Glauber's salt – sodium sulfate with 10 molecules of water, or Na₂SO₄•10 (H₂O) – is also produced. An Aquaclus pilot plant

flowsheet is shown in Figure 1. One of the unique features of the technology was that no ratio control of SO₂ to H₂S was required: it has a fly wheel effect that self-corrects the ratio.

Acid gas (H₂S and CO₂) enters the Aquaclus reactor through a gas distributor, and rich SO₂ solution enters the bottom of the reactor coming from the SO₂ absorber. The solution is below the melting point of sulfur and solid particles of sulfur form immediately. The excess gas and the liquid sulfur slurry flow to the slurry holding tank through separate nozzles. This reaction is as follows:



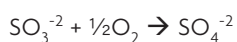
At this point, excess H₂S flows out of the slurry holding tank to the incinerator, where it is converted to SO₂ as per the following reaction:



The incinerator gas is cooled in a waste heat boiler, which causes steam and the newly created SO₂ to flow through an eductor to precool the gases prior to entry into the SO₂ absorption column.

Following the path of the liquid slurry leaving the slurry holding tank, it flows to the intercooler for preheating, then melting of the sulfur in the steam heated heat exchanger and finally phase separation. After phase separation, it flows through the intercooler again, then the fin fan cooler and back to the solution holding tank. Lean solution is sent to the absorber for further SO₂ absorption.

A byproduct, Glauber's salt, is produced from the oxidation reaction as follows:



The sulfate ion must be purged to prevent buildup in the operating solution. This is accomplished with a crystalliser.

Further developments

The technology was developed in Dobbs Ferry, New York, US, at Stauffer Chemical's R&D centre. This facility is now owned by AkzoNobel.

Chesebrough Ponds acquired Stauffer in 1985 while the Queen City facility was still in operation. As part of the sale, all energy-related operations were discontinued. The operating problems had not been solved at this time. Thus, the Aquaclus technology



Figure 3. The sulfur recovery pilot plant in Queen City, Texas, US.

became available for licensing. Darnell Engineering Co. obtained the license in 1986, and immediately initiated a development programme to address the concerns that were ascertained from the Queen City plant operations. This development activity resulted in commercial applications and enabled enhancements to the process to be continued.

The Darnell version, or Modified Aquaclus® technology, produced a particulate sulfur that had to be landfilled, whereas the original Aquaclus produced marketable, bright yellow, molten sulfur that was shipped to a sulfuric acid plant in Houston, Texas. Darnell built two plants, in Tchula, Mississippi, and in Owensville, Texas, neither of which is still in operation.

Tchula

The Tchula plant was installed in November 1987 at a gas conditioning plant operated by TXG Intrastate at a point on its natural gas pipeline. The Aquaclus installation at Tchula processed the sour off-gas from an amine treating system. This off-gas contained approximately 95% CO₂ and 5% H₂S. The Aquaclus plant was designed to process 10 million ft³/d of natural gas, and to produce approximately 6 tpd of sulfur, although the natural gas flow at the Tchula plant had been well below design capacity. This plant exhibited excellent ability to operate below designed volume levels. The Aquaclus installation at Tchula exceeded all requirements imposed by the US Environmental Protection Agency (EPA) and the Mississippi State Air Quality Division.

Owensville

The Owensville plant was installed in May 1988 at a sour gas treating plant owned and operated by

Darnell Engineering. The AquaClaus installation at Owensville extracts sour gases (H₂S and CO₂) from a natural gas stream containing approximately 5.5% acid gas. It has a design capacity of around 1.9 tpd of sulfur.

Complications

The chemistry is sound, the sulfur removal was as expected, the operating costs were in line with projections, but mechanical issues plagued the process. So what went wrong for this technology?

The single well plant had a wellhead pressure decay such that after three days the well had to be shut in for another three days, until there was enough pressure and flow to restart the plant. There was simply no gas flow half of the time.

The three intercoolers in series became plugged with sulfur on the tube side as the sulfur approached its melt point. The velocity in the tubes was less than 3 ft/sec. This created high pressure drop and ever-decreasing flow rate in the circulating loop.

The three intercoolers in series also became plugged with sulfur on the shell side. This was due to carryover of colloidal droplets of molten sulfur. As the cloudy solution cooled on the shell side and sulfur was deposited on the outside of the tubes, the pressure became so high that the flow was too low to operate the plant. The zeta potential (the degree of electrostatic repulsion between adjacent, similarly charged particles in a dispersion) of the colloid was so high that the molten drops of sulfur never coalesced.

Blue precipitate, which was found to be nickel chloride, developed in the circulating solution. This was a minor problem, but chloride-free water must be used for the makeup water in the solution tank on start-up. In fact, deionised water is best.

A new solution

AquaClaus II, a development on the original technology, addresses the above problems. The flowsheet in Figure 2 shows in red the changes to the original process.

For the problem of wellhead pressure decay, there was nothing that could be done. Acidisation of the well was considered but was ruled out since the water table was so close to the hydrocarbon layer. The danger was that if the water coned up around the well perforations, then the well would produce mostly water from that point forward. This could end the project immediately. If the well was not shut in then the intercooler became plugged and went through a melt-out cycle. Actual running time was thus reduced.

Regarding the plugging of the intercoolers, the intercooler itself was the biggest problem. The intercooler, along with the sulfur melting system, was never tested in the bench scale unit. The assumption that sulfur melting was unimportant proved to be wrong; in a bench scale or pilot plant,

all systems and unit operations must be tested. Premelt sulfur is very sticky and this, coupled with low velocity in the tubes, led to plate-out on the inside of the tubes.

The removal of the nickel chloride indirectly solved the shell side plugging problem. A bag filter and two sight glasses were installed on the liquid inlet and discharge on the filter going to the intercoolers, as shown in red in Figure 2. The bag filter acts as a coalescing element. The zeta potential of the molten sulfur droplets was rendered neutral as they flowed through the pores of the bag filter, and streams of bright yellow, liquid sulfur were seen in the sight glass within a clear solution. This was the lean SO₂ solution. The author received US Patent with others for US4631068A – Removal of sulfur from aqueous suspension using filtration. Deionised water must be used for makeup solution preparation so that nickel chloride is not introduced into the system in the first place.

In the new design, a completely new bag filter for a coalescer is integrated into a new tank to handle and catch the additional coalesced sulfur. This is shown in red in Figure 2.

In order to prevent the plugging of the three intercoolers in series, two vertical Klaren BV self-cleaning heat exchangers replaced the three intercoolers, as shown in red in Figure 2. A pumping system with a heat transfer fluid will transfer heat between the two shell sides of the two heat exchangers. Both sulfur plugging streams are on the tube side of each heat exchanger.

The operation of the Klaren self-cleaning heat exchangers works as follows. The fouling-prone fluid that flows upwards inside the tubes is charged with solid particles that are swept upwards, so that the fluid scours the walls of the tubes as they travel. A distribution system in the inlet channel provides a uniform distribution of liquid and particles into all the tubes. From the outlet channel, the particles are carried to the separator where they disengage from the liquid and are returned through the external downcomer into the control channel, and from there through a connecting line into the inlet channel. The flow of particles is activated by the control liquid flow, which is a fraction of the total liquid flow supplied to the exchanger. By changing the control liquid flow, the intensity of the cleaning action can be varied. If desired, the cleaning can also be applied intermittently. However, in the case described, the cleaning is always on.

Conclusion

In conclusion, AquaClaus II can be a viable technology for SRUs. The technological problems experienced in AquaClaus 1 have been eliminated through the use of coalescers to recover the molten droplets of sulfur suspended in the aqueous phase and the use of the Klaren International self-cleaning heat exchangers from the Netherlands. 