Chevron

WWT

WWT
Two-Stage Sour Water Stripping

Improve performance of sulfur recovery units

benefits

THE CHEVRON WWT PROCESS IS A TWO-STAGE STRIPPING PROCESS WHICH SEPARATES AMMONIA AND HYDROGEN SULFIDE FROM SOUR WATERS GENERATED BY PROCESS UNITS IN PETROLEUM REFINERIES. IT PRODUCES STRIPPED WATER, WHICH IS SUITABLE FOR REUSE OR DISCHARGE, AND HYDROGEN SULFIDE, WHICH IS A PREMIUM FEED TO CONVENTIONAL SULFUR RECOVERY UNITS OR SULFURIC ACID PLANTS. AMMONIA MAY BE RECOVERED IN A VARIETY OF FORMS DEPENDING ON APPROPRIATE ECONOMIC JUSTIFICATION.

Why was it developed?

The process was developed partly in response to the stringent environmental restrictions placed upon refineries. Further, Chevron's own experience as a refinery operator showed that relatively simple sulfur recovery plants, such as Claus plants, sometimes could achieve significant performance improvements by keeping ammonia out of the hydrogen sulfide feedstream. The WWT Process emerged from the combination of these pressures and incentives.

Environmentally attractive…

Increasing legislative pressures are being exerted on the refining industry to utilize "best available" technology for protection of the environment. The WWT Process provides the opportunity to economically treat refinery sour waters while producing products that can be safely reused or discharged, sent for further processing, or sold as end products.

Reuse of the stripped water produced by the WWT Process is particularly attractive because it reduces net makeup water requirements and can be an important step toward reducing waste water discharge rates to treating facilities and to receiving waters.

Improved performance of sulfur recovery units…

Separation of ammonia and hydrogen sulfide in a WWT plant has several desirable effects on sulfur recovery units (SRUs):

Eliminates ammonia-related problems such as:

- lower operating factor
- plugging in condensers and seals caused by ammonia salts
- catalyst deactivation

Increase overall sulfur recoveries. Reduces the size of new SRUs and tail gas units by removing the diluent effect of ammonia and the air needed to burn it.

As a corollary effect, incorporating a WWT plant in a refinery processing scheme is an excellent way to debottleneck an existing SRU by removing the ammonia from the acid gas feed.

Ammonia recovery…

The ammonia separated from sour water may be recoverable as a salable product in either the anhydrous or aqueous form. If it is not recoverable, it may be routed to incineration.

Sour water feeds

WWT plant feeds consist primarily of ammonia and hydrogen sulfide dissolved in water, with traces of carbon dioxide, phenol, cyanides and other contaminants present. WWT plants typically have been designed for sour water with ammonia concentrations between 0.3 and 6.0 Wt.% and hydrogen sulfide concentrations between 0.3 and 10.4 Wt.%. The process, however, is not limited to feeds in this composition range; it can handle water with high ratios of ammonia to hydrogen sulfide and also water with high carbon dioxide content. (For example, the WWT Process can handle the high ammonia-containing sour waters produced in shale oil and tar sands upgrading plants and is capable of treating the carbon dioxide containing sour water from shale oil retorting plants.)

WWT plants have successfully processed sour water from many refinery sources:

- hydrocrackers and hydrotreaters
- fluid catalytic crackers
- cokers – delayed and fluid types
- crude units
- amine plants
- flare seals

refining

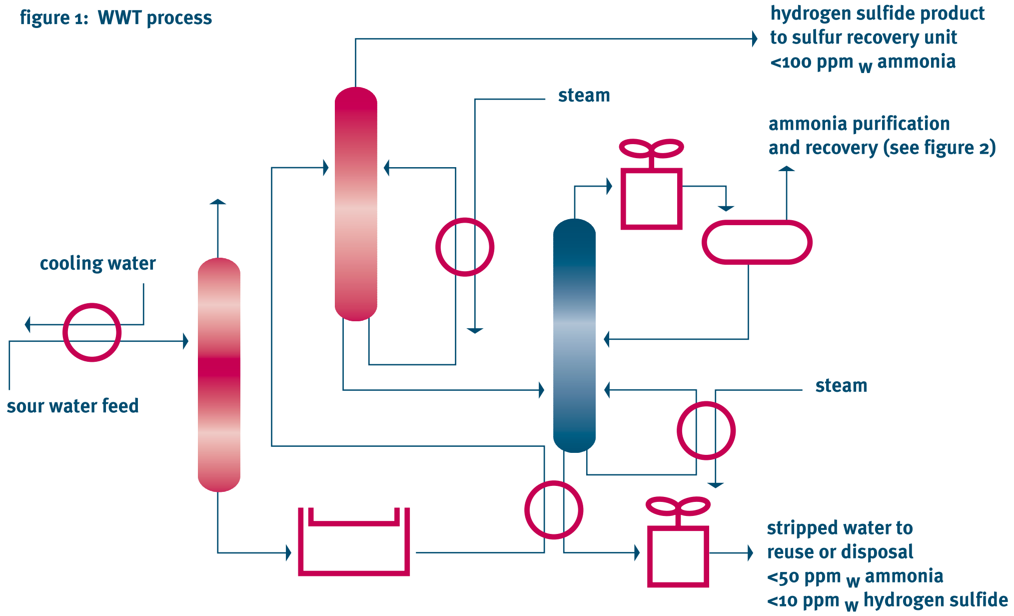
Process description

Figure 1 is a simplified flow scheme showing the four distinct processing steps which embody the WWT Process.

Degassing and feed storage. The sour water feed to the plant, from single or multiple sources, is combined with a recycle stream from the ammonia stripper and is cooled and fed to a degasser where dissolved hydrogen, methane and other light hydrocarbons are removed. The release of acid gas and possible air pollution are minimized. The degassed sour water is pumped to an off-plot storage tank which serves to dampen flow rate and composition changes. The tank also facilitates removal of entrained oil and solids.

Acid gas stripping. From the feed tank, the degassed sour water is pumped to the WWT plant, where it is heated by feed-bottoms exchange and fed to the acid gas or hydrogen sulfide stripper. This stripper is a steam-reboiled distillation column. The hydrogen sulfide, which is stripped overhead, is of high purity – an excellent feed for sulfur or sulfuric acid plants. It contains negligible ammonia and, because the plant feed has been degassed, only traces of hydrocarbons. It does contain, however, any carbon dioxide that is present in the feed.

figure 1: WWT process



Process description (continued)

Ammonia stripping. The hydrogen sulfide stripper bottoms stream, containing all the ammonia in the feed and some hydrogen sulfide, is fed directly to the ammonia stripper, which is a refluxed distillation column. In this column, essentially all ammonia and hydrogen sulfide are removed from the water, which leaves as the column bottoms stream. After exchanging heat with the hydrogen sulfide stripper feed, this stripped water is cooled and sent off-plot for reuse or treating.

The ammonia and hydrogen sulfide stripped from the water in the ammonia stripper are passed through an overhead condenser and are partially condensed.

Ammonia purification and recovery. The vapor product from the overhead condenser in the ammonia stripping section is an ammonia-rich gas which may be handled in a variety of ways, as shown in Figure 2. Selection of the appropriate ammonia recovery option will be totally dependent on the site economics.

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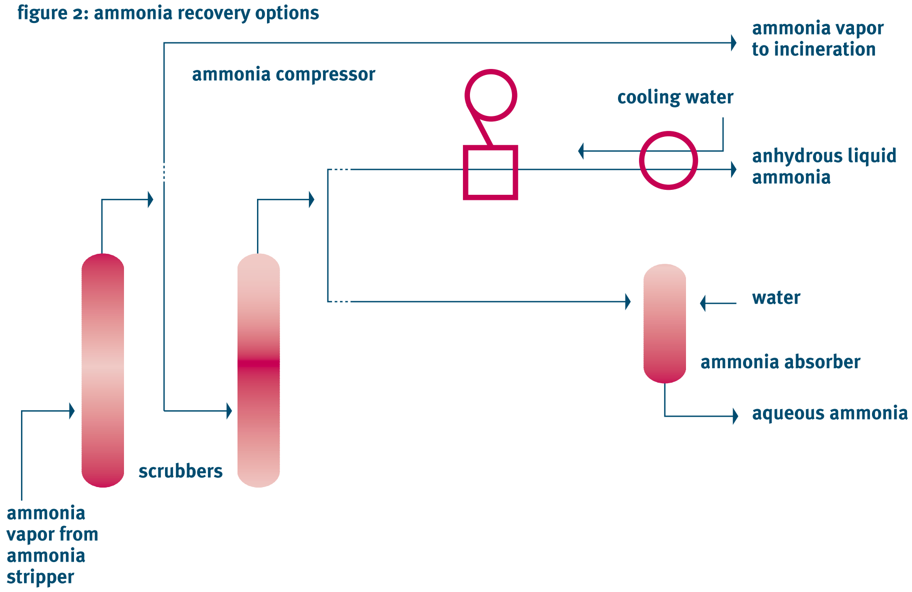
Ammonia incineration

For some plants, actual ammonia recovery may be neither desired nor economical. In such cases, the ammonia product may be incinerated, either directly off the reflux drum or after being scrubbed with water to reduce the hydrogen sulfide content, or it may be further purified and recovered to produce either anhydrous or aqueous ammonia suitable for sale or for further processing.

figure 2: ammonia recovery options



cycling

Anhydrous ammonia

For production of anhydrous ammonia, the gas is first passed through a two-stage scrubbing system to remove hydrogen sulfide. It is then liquefied to produce the anhydrous ammonia.

Aqueous ammonia

For production of aqueous ammonia, a one- or two-stage scrubbing system may be used to remove the hydrogen sulfide. The ammonia gas is then dissolved in water to yield the desired product grade.

products

TYPICAL INSPECTIONS OF PRODUCTS FROM THE WWT PROCESS ARE SUMMARIZED IN TABLE I. WWT PLANTS CAN BE DESIGNED TO SEPARATE/RECOVER A RANGE OF DESIRED PRODUCT QUALITY – IN FACT, ACTUAL PRODUCT INSPECTIONS ARE GENERALLY BETTER THAN THOSE WE QUOTE AS TYPICAL.

Hydrogen sulfide

The hydrogen sulfide product will typically contain less than 100 ppm of ammonia, with only traces of hydrocarbons. Any carbon dioxide present in the sour water feed will remain in the hydrogen sulfide product.

The hydrogen sulfide is generally available at about 100 psig (6.9 Bar) and 100 °F (38 °C) and is saturated with water vapor.

Table 1 – Typical product inspections from the WWT process

	hydrogen sulfide	stripped water	anhydrous ammonia
form	gas	liquid	liquid
ammonia, ppm	< 100	< 50	
hydrogen sulfide, ppm		< 10	< 5
mercaptan sulfur, ppm			2–5
oil, ppm			5–15
water, wt. %			0.4
temperature, °F (°C)			100 (38)
pressure, psig (Bar)			200 (13.8)

Stripped water

The stripped water typically contains less than 50 ppm of free ammonia and less than 10 ppm of free hydrogen sulfide.

It also will contain traces of phenols and salts which entered with the feed. If the feed contains acidic compounds that “fix” ammonia, the fixed ammonia can be released and then stripped off.

Stripped water produced by the WWT Process may be reused or discharged through downstream treating facilities without problems. It has many reuse possibilities, including hydroprocessing unit injection water, crude unit desalter water and process water wash. For example, stripped water from WWT plants has been successfully reused in ISOCRACKING plants (the Chevron licensed hydrocracking process). WWT stripper water has been used successfully for many years as hydrocracker injection water.

The reuse of WWT water is particularly attractive because it reduces net makeup water requirements and can be an important step toward reducing waste water discharge rates to treating facilities and to receiving waters.

Ammonia

Ammonia produced as vapor for incineration will typically be scrubbed to reduce the hydrogen sulfide content to about 1500 ppm. The ammonia will be saturated with water at the scrubber temperature.

Under normal operating conditions, anhydrous liquid ammonia will have maximum free hydrogen sulfide and water contents of 5 ppmw and 0.4 Wt.%, respectively. Typical conditions at the plot limit are a temperature of 100°F (38°C) and a pressure of 200 psig (13.8 Bar). The anhydrous ammonia will contain trace amounts of mercaptans and oils. WWT-derived ammonia must be analyzed to check for conformance to end-use sales specifications.

The WWT Process has the flexibility and versatility to meet the needs of the refiner. In particular, a plant can be designed to economically handle large volumes of dilute sour water, to reuse appropriate existing equipment and to meet a phased construction requirement.

Handling very dilute sour waters

Where large volumes of dilute sour water need to be handled, it is often economic to concentrate very dilute sour waters in a separate preconcentrator column preceding a two-stage WWT plant. The concentrated sour water overhead stream from the preconcentrator is sent to the WWT feed tank where it is mixed with other sour water streams (to dampen flow rate and composition changes) before being fed to the WWT plant.

The preconcentrator produces stripped water of the same quality as that from a two-stage WWT plant.

flexibility

Reuse of existing equipment… for preconcentration

In many cases, existing refinery sour water strippers (SWS) can be easily converted to sour water concentrators. This can result in significant cost savings by reducing the size of the two-stage WWT plant. Not only is investment reduced, but utility costs also are reduced because of lower steam and cooling water consumption. The three-column approach to WWT plant design using existing SWS columns has been implemented successfully in three of Chevron's own refineries as well as in several licensee plants.

…for ammonia or hydrogen sulfide stripping

An existing SWS column and its associated equipment may be used in the ammonia or hydrogen sulfide stripping sections of the standard WWT design. Careful review of the SWS column design pressure and internals, together with the design duties of reboilers, heat exchangers, condensers, etc., is essential to ensure compatibility with WWT design requirements.

Phased construction

The WWT Process has the flexibility to be implemented in two phases. In certain situations this may be desired. It can be achieved by designing and installing only the ammonia stripper column of the WWT and operating it initially as a sour water stripper. Then, when the situation and economics dictate, it can be integrated into a WWT plant. The design of the plant is completed by the addition of a hydrogen sulfide stripper, appropriate ammonia purification equipment and other auxiliary equipment.

efficiency

Plant references

The WWT Process has been in commercial service since 1966. Like most processes which Chevron offers for license, WWT was developed to meet the needs of our own operating refineries. Only after it was proved in Chevron service was it offered to the industry. As a result, Chevron operates the oldest WWT Process plants as well as some of the newest. Thus, we are familiar with the long-term performance of these units and have an operator's continuing concern for their safety and reliability.

expertise

Technology transfer

Chevron offers WWT Process technology in a flexible and commercially proven package for a wide range of sour water processing needs. Chevron has process, control and materials know-how based on 300+ years of commercial plant experience. Additionally, Chevron can design integrated sour water stripper (SWS) and WWT schemes, thereby providing a comprehensive and economic solution to the toughest sour water problems.

Technical service

Chevron Research Company offers reliable and responsive technical service in support of the WWT Process under the terms of a technical service agreement. A variety of services is available:

- process design for construction
- process and analytical manuals
- front-end engineering design (optional)
- review of contractor's mechanical design
- plant inspection and startup assistance
- operator training, including a PC-based WWT
- process simulation package
- ongoing technical service

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