

Application Note AN-PAN-1001

Online analysis of hydrogen sulfide and ammonia in sour water stripper

Sour water refers to the wastewater stream generated at many locations within a refinery, but specifically from crude distillation (CDU), fluid catalytic cracking (FCC), catalytic reforming, coker, and acid gas removal units [1]. Thus, this stream contains contaminants such as hydrogen cyanide (HCN) and carbon dioxide (CO $_2$), but most importantly hydrogen sulfide (H $_2$ S) and ammonia (NH $_3$). These contaminants can be highly corrosive and detrimental to company

assets; therefore, they need to be removed at a sour water stripping plant (SWS) before the stripped sour water (SSW) of effluent can be reused in the refinery. This Process Application Note details the simultaneous online analysis of H₂S and NH₃ in sour water which was previously treated in the sour water stripper (SWS). The method includes automatic cleaning and calibration. Fast and accurate results are continuously supplied for process control.

INTRODUCTION

«Sour water» is condensed wastewater produced during many downstream refining processes containing hydrogen sulfide, ammonia, and other contaminants. It is often acidic in nature and can cause corrosion problems within the refinery's pipework so must be treated before it can be reused or disposed to the waste treatment plant.

The sour water is treated in a sour water stripper

(SWS) that uses a steam stripping process to remove sulfides and ammonia as gases. The sour water is received directly from the refinery to the flash drum as part of the «degasification» step (Figure 1). In there, the remaining light hydrocarbons are removed or «flashed off» from the water. The sour water is then stabilized in a tank before it is heated and sent to the stripper column.

$H_2S + NH_3 \rightleftharpoons NH_4SH \rightleftharpoons NH_4^+ + HS^-$

Reaction 1. Chemical decomposition reaction in a stripper column

At optimum pH, the sour water mixes with steam and the ammonia and hydrogen sulfide gases vent to the top of the stripper column to the Sulfur Recovery Unit (SRU). This separation happens due to the difference within the components' boiling points. The stripped water is either used to produce steam in the reboiler or pumped within control limits to the wastewater treatment plant for further processing.



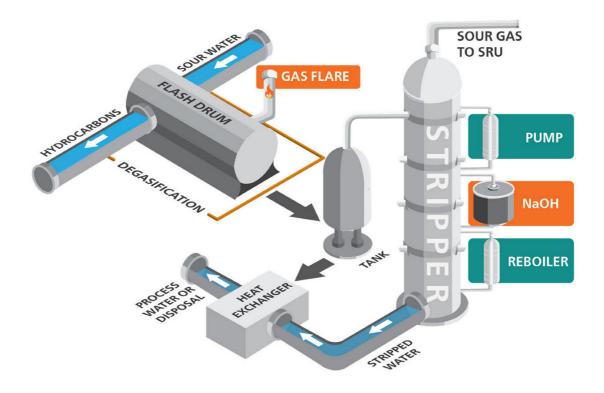


Figure 1. Sour water stripping process scheme (SRU: Sulfur Recovery Unit).

Monitoring $\rm H_2S$ and $\rm NH_3$ content in stripped sour water is necessary to guarantee stripping efficiency and verify if the wastewater can be recycled or released to the environment.

The poisonous conditions of this process make manual sampling for analysis a challenge since human intervention is needed to adapt current operation conditions to the process. Thus, online and inline analysis solutions are preferred.

In order to ensure an adequate extraction of H₂S from the stream, it should be constantly monitored online. In the same way, optimization of the ammonia stripping efficiency should be extensively monitored to avoid the formation of ammonium (NH₄⁺), which cannot be stripped as a gas. Therefore, caustic (NaOH) is injected at the bottom of the tower to keep the pH above 8, facilitating NH₃ gas formation. Online analysis of ammonia and sulfides will increase the «stripper efficiency» of the SWS, leading to significant steam reduction and increased energy savings. Effectively stripping and monitoring H₂S and NH₃ is also an essential operation in the overall pollution reduction program of refineries.



APPLICATION

The 2060 Process Analyzer can analyze H₂S and NH₃ simultaneously with automatic cleaning and calibration steps using absolute wet chemical techniques. Sulfide (S²⁻) is determined by a precipitation titration with silver nitrate (AgNO₃). Ammonia is determined by Dynamic Standard Addition (DSA). Fast and accurate results are continuously transmitted to the programmable logic controller (PLC) for process control.



Figure 2. 2060 Process Analyzer for online analysis of ammonia and hydrogen sulfide in the sour water stripping process.

Table 1. Parameters to monitor in SWS effluent.

| Analyte | Concentration (mg/L) |
|------------------|----------------------|
| NH ₃ | 0–200 |
| H ₂ S | 0–50 |

REMARKS

Other contaminants that increase the sour water corrosiveness like phenol and cyanide can also be

analyzed with Metrohm Process Analyzers.

FURTHER READING

Brochure: Petroleum and Petrochemicals Industry
Mercaptans and hydrogen sulfide in raw oil in
accordance with ASTM D3227 and UOP163

<u>Determination of salt in crude oil</u> <u>Online thermometric titration of acid number (AN) in</u> <u>oils (ASTM D8045)</u>

BENEFITS FOR TITRATION IN PROCESS

- **Protection of company assets** with built-in alarms at specified warning limits to prevent corrosion
- Safer working environment for employees (corrosive environments)
- **Guarantee compliance** with environmental standards
- Lower energy cost by avoiding over stripping of ammonia and sulfide





REFERENCE

1. Sour Water Stripping (SWS) - Oil & Gas | Pall Corporation https://www.pall.com/en/oil-

gas/refining/sour-water-stripping.html (accessed 2021-10-05).

CONTACT

Metrohm Nederland Bijdorpplein 13-15 2992 LB Barendrecht

info@metrohm.nl



CONFIGURATION



2060 Process Analyzer

The 2060 Process Analyzer is an online wet chemistry analyzer that is suitable for countless applications. This process analyzer offers a new modularity concept consisting of a central platform, which is called a «basic cabinet».

The basic cabinet consists of two parts. The upper part contains a touch screen and an industrial PC. The lower part contains the flexible wet part where the hardware for the actual analysis is housed. If the basic wet part capacity is not sufficient enough to solve an analytical challenge, then the basic cabinet can be expanded to up to four additional wet part cabinets to ensure enough space to solve even the most challenging applications. The additional cabinets can be configured in such a way that each wet part cabinet can be combined with a reagent cabinet with integrated (non-contact) level detection to increase analyzer uptime.

The 2060 process analyzer offers different wet chem techniques: titration, Karl Fischer titration, photometry, direct measurement and standard additions methods.

To meet all project requirements (or to meet all your needs) sample preconditioning systems can be provided to guarantee a robust analytical solution. We can provide any sample preconditioning system, such as cooling or heating, pressure reduction and degassing, filtration, and many more.

