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_2S) 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 H_2S and NH_3 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.

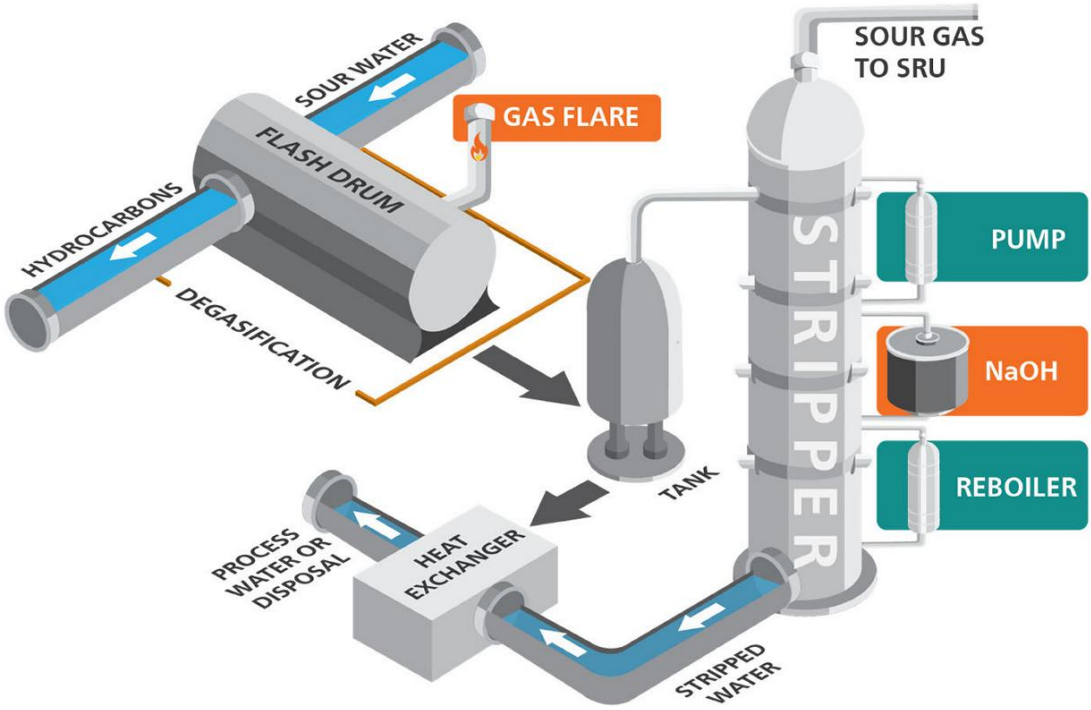

Figure 1. Sour water stripping process scheme (SRU: Sulfur Recovery Unit).

Monitoring H_2S and 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 H_2S 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 (NH_4^+), 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 NH_3 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 H_2S and NH_3 is also an essential operation in the overall pollution reduction program of refineries.

APPLICATION

The 2060 Process Analyzer can analyze H_2S and NH_3 simultaneously with automatic cleaning and calibration steps using absolute wet chemical techniques. Sulfide (S^{2-}) is determined by a precipitation titration with silver nitrate ($AgNO_3$). 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_2S	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

Determination of salt in crude oil

Online thermometric titration of acid number (AN) in oils (ASTM D8045)

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).

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