

Inorganic Scale Issues and Treatment for Sour Water Strippers

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ABSTRACT

During oil and gas operation, water is used for many operation processes, which make water contain various contaminants depending on the sources and processes. Sour water strippers (SWS) are critical units to remove ammonia (NH_3) and hydrogen sulfide (H_2S) from sour water streams to condition the waters for the discharge or reuse. Different streams from various sources may induce different scale issues to cause operation productivity reduction and even equipment failure. The most common scales in sour water strippers are calcite, iron sulfite, silicates, etc. depending on the water chemistry of source streams.

This paper presents case histories of scale issues and treatment of sour water strippers with various source waters. For each case history, the specific inorganic scale problems and treatment strategies are discussed. Based on the lab testing and field application results, scale inhibitor treatment or even cleaning-up program are evaluated.

This paper provides valuable information on potential scale problems and treatment for sour water strippers with various water sources, and gives references or guideline for similar scale treatment.

Keywords: Sour Water Strippers, Scale Treatment, Cleaning-up

INTRODUCTION

Sour water stripping is used to remove ammonia (NH_3) and hydrogen sulfide (H_2S) from sour water streams coming from many operation units to condition it for discharge or reuse.¹⁻³ In a complex refinery, most of the sour water comes from distillation, fluid catalytic cracking, catalytic reforming, coker and acid gas removal units, with many other operations contributing to the balance. The different streams are usually collected in a surge tank for centralized processing via a heat exchanger and a single stripper column, or two in series.

A combination of pH control and heat, from direct injection steam or reboiler drives off the ammonia and hydrogen sulfide. The presence of solids and hydrocarbons ('oils') are major contaminants in the units of heat exchanger, stripper column, and reboiler fouling. These fouling will cause the loss of SWS capacity and may bottleneck refinery production rates, drive the need for unscheduled SWS shutdowns and cleanouts leading to additional production losses, high maintenance costs and increased worker safety issues from exposure to the highly volatile H₂S in the sour water system.

This paper presents several case histories, including the stream sources with product water and refining water, at different refinery locations with scale types of barite, ZnS, calcite, silicates, etc. The laboratory tests were conducted under mimic field conditions for product performance evaluations. This paper provides valuable information on potential scale problems and treatment for sour water strippers with various water sources, and gives references or guideline for similar scale treatment.

EXPERIMENTAL PROCEDURE

Scale prediction modeling

Scaling tendencies were estimated using the scale modeling software program ScaleSoftPitzer™ version 2021 (SSP2021), a software package developed by the "Brine Chemistry Consortium" at Rice University.

Scale prediction yields both the scaling potential expressed as the saturation index (SI) and the scaling severity that is associated with the potential amount of precipitation in mg/L of a concerned scale at system conditions. The SI is a measure of the degree of super saturation of the scaling ions in an aqueous system and an indication of the driving force for the supersaturated scaling ions to form scale. SI is defined as the logarithm of the ratio between scaling ion activity product and the thermodynamic solubility product of a concerned scale. In other words,

- SI < 0 the concerned scaling ions are under-saturated (no scale formation)
- SI = 0 the scaling ions are at the saturation/equilibrium level
- SI > 0 the scaling ions are supersaturated (tend to form scale)

The greater the SI, the stronger the driving force promoting the precipitation of scaling ions, and generally once initiated the faster the precipitation process.

The amount of equilibrium precipitation (mg/L) is the maximum amount of scale that would precipitate out of solution when the scaling ions reach the saturation/equilibrium level from the initially supersaturated state. It indicates the mass of scale that could potentially precipitate from supersaturated brine. It should be noted that the accuracy and reliability of the scale prediction results depend on the factors such as the accuracy of both the produced water chemistry data and production conditions that were used as input to the software package, as well as the correctness of the prediction model itself.

Kinetic Turbidity Tests

The Kinetic Turbidity Test is conducted with an Agilent Cary 100/300 series ultraviolet-visible (UV-Vis) spectrophotometer, which measures the absorbance of the sample solutions at a certain wavelength. Up to 12 samples are under temperature control, in a multi-sample holder with magnetic stirring in all cells. The samples can be tested simultaneously at temperatures ranging from 4°C to 95°C with designed cuvettes that are usually made of quartz. Each cuvette has a small hole on the bottom to hold a small magnetic stir bar.

To conduct the test, a cuvette was placed in the first cell holder with 3 mL of deionized water to establish the baseline for turbidity. Anion brine is first added to the sample cuvettes. Various

concentrations of inhibited anion brine are then added to each of the remaining cuvettes. Immediately before the start of the test, cation brine is then added to each of these cuvettes. The spectrophotometer reads results every 2 minutes, with a 5-second measurement time per cuvette over a 2-hour period. Testing can be longer based on the testing requests.

The kinetics application uses the absorbance versus time data to determine the rate of reaction. This function records scale formation kinetics and differentiates scale inhibitor performance by observing how fast absorbance increases. The faster the absorbance observed, the faster the scale formation.

Aerobic Bottle Tests

Aerobic bottle test was conducted with synthetic brine based on waters from the sour water stripper water analysis. Cation and anion solutions of each brine were prepared. Each anion solution was adjusted to the designed pH by purging CO₂ and N₂. After that, 50 mL anion solutions were put into a series of 4 oz. bottles, then the desired amount of scale inhibitor was dosed into bottles. After shaking thoroughly to mix anion solution and scale inhibitors, 50 mL cation solutions were added to each bottle, and these bottles were immediately inverted several times to assure thorough mixing of the components. Control and blank samples were also prepared. The control sample contained the mixture of same volume of cation solution and deionized water to simulate the case without scale formation. The blank sample contained equal mixtures of anion and cation water to represent a brine with no protection against scale formation. All bottles were capped and placed in an oven with the designed heating temperature for a period of 24 hours. Visual observations of the resulting inhibited solutions were made initially and 24 hours after the addition of each scale inhibitor.

Chemicals and Materials

Fe₂O₃ is from Alfa Aesar 97% (trace metals basis), and surface area is 11.60 m²/gram, 325 mesh powder. Na₂SiO₃·5H₂O, NaCl, CaCl₂·2H₂O, etc. are from Fisher Scientific, ACS certified grade.

The inhibitors in this paper are:

- Product A: a phosphonate inhibitor + a polymer inhibitor;
- Product B: a phosphonate inhibitor + a silicate inhibitor;
- Product C: a polymer inhibitor;
- Product D: a phosphonate inhibitor + a silicate inhibitor;
- Product E: a silicate inhibitor;
- Product F: a phosphonate inhibitor + polymer inhibitor;
- Product G: a phosphonate inhibitor + a polymer inhibitor;
- Product H: a phosphonate inhibitor;
- Product I: a phosphonate inhibitor;
- Product J: a phosphonate inhibitor;
- Product K: a polymer inhibitor.

CASE HISTORIES

Introduction of sour water stripper

Sour water stripping is the common method used in refineries to remove contaminants from sour water before further treatment in other units or discharge into the effluent system. Primary contaminants are ammonia, hydrogen sulfide, mercaptans, phenols, cyanides, and other compounds regulated by various pollution control authorities.

There are several varieties of sour water strippers. All of them operate by passing the sour water downward through a multistage tower while an upward flow of stripping gas removes the contaminants. Tower internals may be trays, packing, or other contacting devices. Stripping gas is usually steam,

although flue gas, fuel gas, or air can be used. Figure 1 shows the diagram of a typical sour water stripper.

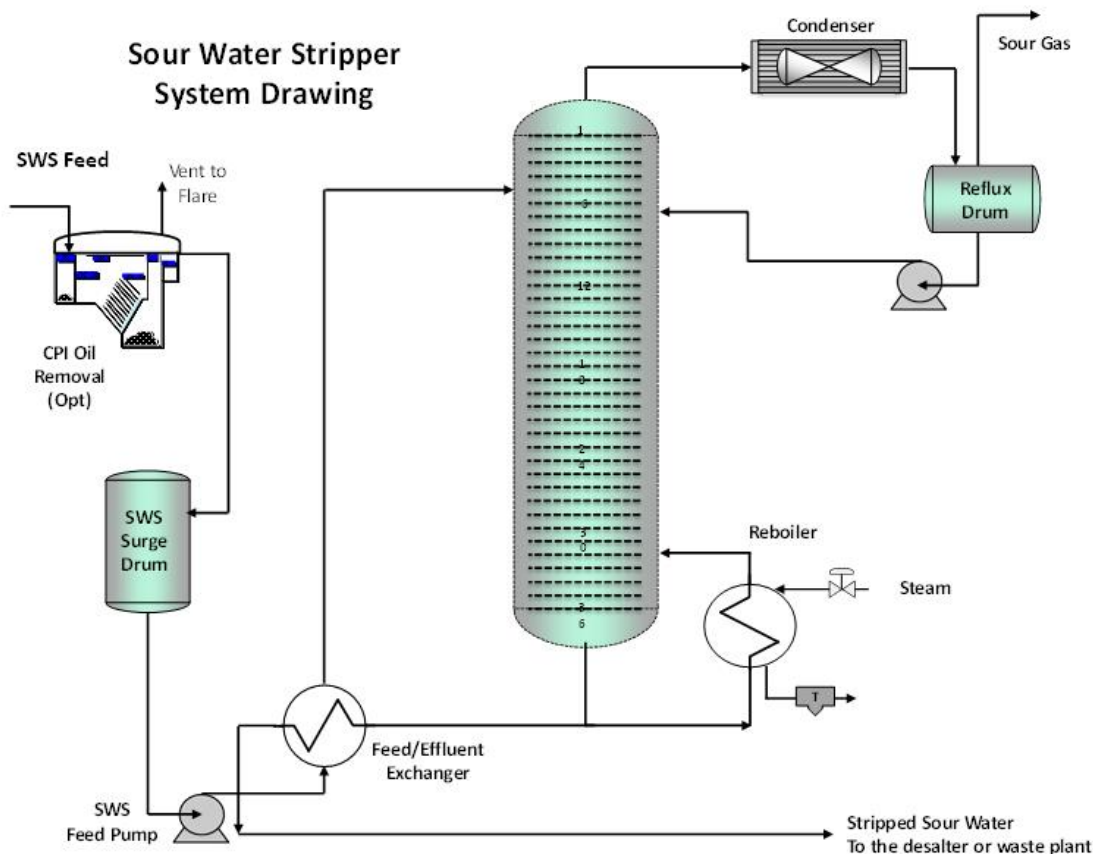


Figure 1: Diagram of a sour water stripper.

Based on two major operation applications, gas processing and refining, several types of water sources for the influx of sour water strippers are described in this paper:

1. For gas processing, the water sources include:⁴⁻⁶
 - a. Product water: Water originated in the reservoir and flowed up the tube with gas, having high TDS and hydrocarbons;
 - b. Condensed water: it is also called “salt free water” that condenses from the gas after the gas has left the producing reservoir;
2. For refining:⁷⁻⁸

Waters from the refining units, including desalts, crude/vacuum units, hydrotreaters, FCCs, thermal cracking, hydrocracking, Amine treating, etc.. They typical contain H₂S at the range of 300-12,000 ppm, and NH₃ at the range of 100-8,000 ppm with pH: 8-10.

Different water sources contain various amount of dissolve ions. When entering sour water strippers, the changes of system conditions, including temperature, pH values, the presence/stripping of gas, etc., cause different types of scale formation, which requests different treatment chemicals and strategies.

Produced water as feed water

1. Sour water stripper with barite and ZnS issues

The paper SPE-200693-MS presents a case history on scale formation of barium sulfate and zinc sulfide in a produced water stripper (PWS). Initially, Product A was injected into the feed water and

sulfuric acid is injected about 2 feet downstream, to control the pH to about 7.5. However, deposits were found in the stripper. Better treatment program was requested due to the accumulated deposit amount in the system.

The water analysis of product water from different collection time is shown in Table 1. The waters contain high levels of barium, sulfate, and H₂S. The scale modeling was conducted by ScaleSoftPizter 2021, and modeling results in Table 2 show that the major scales are barium sulfate and ZnS, which agrees with the deposit analysis.

Table 1
Brine Composition

Ions	Unit	Brine 1	Brine 2
Na ⁺	mg/L	7,823.73	9,940.0
K ⁺	mg/L	-	1,379.0
Mg ²⁺	mg/L	3.60	0.71
Ca ²⁺	mg/L	42.50	8.31
Sr ²⁺	mg/L	-	8.51
Ba ²⁺	mg/L	4.89	78.00
Zn ²⁺	mg/L	0.56-5.6	1.0
Cl ⁻	mg/L	12,064.00	15,700.0
SO ₄ ²⁻	mg/L	2,976.00	2,940.0
HCO ₃ Alkalinity	mg/L as HCO ₃	557.50	2,625.0
H ₂ S(aq)(calculated)	mg/L	250	250.0
pH, measured (STP)	pH	7.51	7.50
TDS	mg/L	23,630.54	36,694.74

Table 2
Scale Prediction Based on the above Water Analysis

Brine	Temp.	Pres.	Calculate pH	Barium	Barite		ZnS		Calcite	
	°F	psia			SI	mg/L	SI	mg/L	SI	mg/L
Brine 1	185	14.7	7.5	4.89	2.46	8	12.13	8.35	-	-
	185	14.7	4.0	4.89	2.46	8	5.88	8.35	-	-
	185	14.7	7.5	1.12	1.82	2	12.13	8.35	-	-
Brine 2	203	14.7	7.5	78.0	2.83	132	9.35	1.5	0.60	15

The experimental testing details can be found in the paper SPE-200693-MS⁹. For the scale treatment, Product A was selected by precious experience, and no tests was conducted. After the field trial, it is found that Product A cannot effectively prevent barite and ZnS formation. In order to select the effective scale inhibitors, based on field application conditions, three rounds of testing were conducted. The first round of testing was to screen the best fit chemistry for the applications by kinetic turbidity tests and bottle tests, and PRODUCT C was selected for the field application. After the field trial, Product C was proved to have better performance than Product A. Then the product dosage optimization was requested by operation. The second round of testing were conducted to optimize the dosages of PRODUCT C for the treatment based on the updated operation conditions. At the same time, more cost-effective inhibitors were also requested. The third round of testing were to find more effective chemicals on the field applications. For the third rounds of testing, a series of products of phosphonate inhibitor, polymer inhibitor or their combination were selected for the testing by KTT, aerobic bottle test and anaerobic bottle test. Based on the testing results, the phosphonate inhibitors work better for barite inhibition, and polymer inhibitors work better on ZnS dispersancy and inhibition. The combination of these two inhibitors can more effectively prevent both barite and ZnS formation. The recommended product for the treatment is Product F, which has good performance for both barite and ZnS inhibition and dispersancy.

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