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"Stripped sour water reuse at an Oil Refinery''. Case Study and an Economical Evaluation.

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ABSTRACT

Many opportunities are studied to decrease the overall water balance to achieve sustainability and water management of the petroleum sector, and this can happen by applying modern methods of conservation/reuse and recycling. Various sources of waste water are generated in the petroleum oil refineries , and contaminates are the restricting factor of water reuse .Oil refineries generates large volumes of sour water, which contains high concentrations of contaminants such as oil, grease, ammonia, hydrogen sulfide and dissolved solids. Traditionally, this water is treated and then discharged to the surface water bodies causing a negative environmental impacts. Contaminants in sour water can be treated to make it reusable in a valuable processes as washing water for air coolers instead of condensate water due to the high cost and availability of condensate. This study explores the feasibility of using refinery treated sour water as a supplement source for condensate water in the (REAC) wash. The goal is to evaluate the technical and economic viability of this approach, as well as its potential environmental benefits. The results of this study show that using refinery treated sour water is a viable option for air cooler wash water. The treated sour water meets the required quality standards for this application, and its availability is not affected by the process requirements that limit the availability of condensate water. Moreover, using treated sour water can reduce water consumption and wastewater discharge, resulting in cost savings and environmental benefits.

Keywords: Stripped Sour Water- Water reuse- REAC(Reactor Effluent Air Cooler) - Condensate water wash-Treated water-Environmental Regulations-Economical evaluation

1. INTRODUCTION:

The petroleum refining industry is one of the largest water-consuming industries in the world, with water being used for various processes such as cooling, steam generation, and crude oil processing. As global demand for petroleum products continues to rise, so does the demand for water by the industry. This has led to water scarcity issues in many regions where petroleum refineries operate, particularly in areas with limited water resources or regions experiencing drought conditions (ABUMOGHLI, 2019) [1].

In addition to the issue of water scarcity, the petroleum refining industry also faces regulatory pressure to reduce its water usage and wastewater discharge, as well as growing public concern over the environmental impact of its operations. As a result, there is a need for sustainable water management practices in the industry that can help reduce water consumption, (LOUIS E.OTTIS, 1964) [2] minimize wastewater discharge, and improve the overall sustainability of the industry.

One potential solution to this issue is the use of refinery treated sour water as a replacement for condensate water as Reactor Effluent Air Cooler REAC wash water. Sour water is a byproduct of the refining process and contains high levels of contaminants such as oil, grease, and dissolved solids. Traditionally, this water is treated and then discharged, often to surface water bodies, which can have negative environmental impacts. Alternatively, condensate water has been used as wash water for Reactor Effluent Air Cooler REAC, but its availability and cost of production can be limited due to process requirements (HUSSAIN, 2023) [3].

However, using treated sour water as air cooler wash water offers several potential benefits. It can reduce water consumption and wastewater discharge, as well as provide a sustainable water management solution for the industry. Treated sour water can be treated to meet the required quality standards for air cooler wash water, and its availability is not affected by the process requirements that limit the availability of condensate water. Moreover, it can reduce the environmental impact of the industry by reducing the discharge of treated wastewater into surface water bodies.

The use of refinery treated sour water as Reactor Effluent Air Cooler REAC wash water is an emerging concept that requires further research to evaluate its technical and economic feasibility, as well as its potential environmental benefits. However, it is a promising approach that could help the petroleum refining industry reduce its water footprint and improve its sustainability.

By implementing sustainable water management practices, the industry can continue to meet the growing demand for petroleum products while minimizing its impact on the environment and preserving water resources for future generations.

Refinery sour water originates largely from Crude overhead boot water, delayed cokers, Hydrodesulphurization reactor effluents, fluid catalytic cracking units & visbreaker fractionators. The main contaminants are NH_3, H_2S, Oil, Chlorides (Pedro D.A. Bastos a b c, 2020)[4].

Sour water stripper bottoms are reused in four places:

1. First as a Wash water for the crude desalter on a once-through basis, to remove chloride salts that promote HCl evolution in the crude tower overhead condensers and recover Phenol from wash water to the Crude from the wash water to be treated in the process units again with an extent that can reach up to 90% phenol recovery to the Crude (IPIECA, 2010)[5], See Figure 01.
2. Second as a Make-up water for hydrotreater effluent recycles wash water to remove ammonia sulfide salts that plug the downstream condensers.
3. Third as a Crude overhead wash water circulation to increase the water dew point temperature & to remove salt deposits in air coolers.
4. Fourth as a Flare water Seal instead of Service.

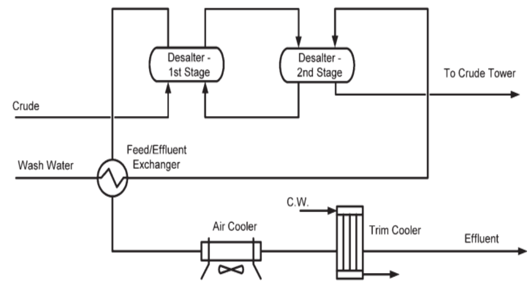

Figure 01: Crude Washing Diagram

When sour water stripper bottoms are used in the crude desalter, the NH_3 content should be about 50 ppm. Higher NH_3 levels interfere with crude unit corrosion control due to chlorides presence.

The ideal pH value for stripping H_2S is below 5 since above 5, sulfide is primarily found in the form of ions (HS- or S-2). Alternatively, efficient ammonia stripping requires a pH above 10 to prevent the formation of ammonium (NH_4+) ion that cannot be stripped. Although the most favorable strategy for sour water stripping is a three-step process where two separate stripper towers are used, one for removing hydrogen sulfide and the other for removing ammonia, the economics usually dictates a compromise. Having only one stripper tower and using a pH around 8 allows adequate removal of both gases.

A solution of NH_3 and H_2S in water. The composition is given in the material balance. The NH_3 and H_2S are present in the aqueous solution as NH_3SH, which is the salt of a weak base (NH_4OH) and a week acid such as the H_2S. In the solution, this salt is hydrolyzed to form H_2S and NH_3.

$$NH4SH \longleftrightarrow H2S+NH3$$

(NH4+ SH)

The **equilibrium constant** is:

$$KH= (H_2S)\ (NH_3)/\ (NH_4+)\ (SH-)$$

H_2S and NH_3 are dissolved physically. Therefore, the releasing of these gases is favored by decreasing pressure and increasing temperature of the solution. This process is done in the stripping tower with the assistance of a reboiler which vaporizes the water at the bottom (Mosher, 2008)[6].

The stripper is designed with a reflux of the overhead condensed vapors, being the final NH_3 and H_2S content of the stripped water influenced by this reflux ratio. The maximum concentrations of H_2S and NH_3 are:

H_2S…………………10 ppm (mol)

NH_3 …………………50 PPM (mol)

2. SOUR WATER TREATMENT STEPS:

The process of treating sour water to meet the required quality standards for air cooler wash water involves several steps, see Figure 02:

1. Separation: The 1st step is to separate the sour water from any oil, grease, or solids that may be present. This is typically done using gravity separation typically a three phase separator.
2. Contaminants Removal: The 2nd step is done by stripping of contaminants like NH_3 and H_2S by using Low pressure steam (LPS) this step can be done on one step on one tower or 2 towers. The LPS stripping step causes the decrease of the partial pressure.
3. pH Adjustment: The pH of the sour water is then adjusted to a suitable range to facilitate subsequent treatment processes. Typically, the pH is raised using a caustic soda solution.

Once the sour water has been treated (Dr. Ing. Mariana Siwek, Sepetmber,2011)[7], it is tested and evaluated for its suitability as air cooler wash water. The water is typically tested for various parameters such as pH, NH_3, H_2S, Chlorides, and Phenol to ensure that it meets the required quality standards for air cooler wash water and crude washing in the Desalter.

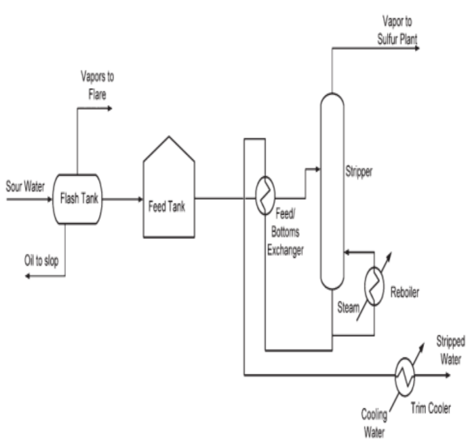

Figure 02: Treatment process of Sour Water Treatment Unit

The treated water is also evaluated for its suitability in terms of its impact on the Air coolers. This involves testing the water's corrosiveness and scaling potential, as well as its ability to dissolve the ammonium sulfate/bisulfate to avoid plugging the air coolers tubes, to be returned in the sour water to be treated in the Sour Stripping Treatment Unit.

To test the water's reuse suitability or to be discharged to the waste water treatment unit, samples of the treated water are exposed to metal coupons for a specified period of time and then analyzed for any signs of corrosion. Overall, the treated water must meet the required quality standards for air cooler wash water, be non-corrosive, have a low scaling potential, and provide effective cooling of the air coolers. By testing and evaluating the treated water in these ways, the suitability of the treated sour water for use as air cooler wash water can be determined.

3. RESULTS AND ANALYSIS:

The quality of the sour water feed to the unit and the treated sour water Produced can represents the capability of reuse. The suitability for use as an air cooler wash water dependable on the amount of contaminants present on the treated stripped water. The analysis table represents the analysis for all contaminants in the feed and product, the analysis was done for one year and the results was represented for the complete evaluation as Min, Max and Average.

All contaminants represented Table 01/02 represents the capability of the unit for the stripping the NH_3/H_2S contaminants to the acid gas treatment. It is worth mentioning that further treatment of the acid gas is done in sulfur recovery unit to completely destroy the ammonia by burning on the thermal reactor above 1428°c and the H_2S is converted to liquid sulfur in thermal reactor and the catalytic converter to be solidified in the sulfur solidification packages.

The SWS (Sour Water Stripping Unit) is considered one of the important environmental treatment units that is very useful for the Oil Refineries beside the Amine treatment Units and the SRU (Sulfur Recovery units). The information of the cost savings and environmental benefits associated with using treated sour water instead of condensate water is going to be discussed in the chapter 4 discussion.

- **Sour water Analysis for feed / products for TR01/TR02**

Table 01 Sour Water Stripping Train01 Analysis

Feed Sour Water TR01	Method	Max. ppm	Min. ppm	Average ppm
NH3	UOP 740	9435.0	1812.0	4674.1
H2S	APHA 4500SD	10500.0	5000.0	9013.8
Oil Content	ASTM D7066	15000.0	1000.0	3354.8
Product Stripped Water TR01	Method	Max. ppm	Min. ppm	Average ppm

NH3 **(50 max.)**	UOP 740	32.0	10.0	20.5
H2S **(10 max.)**	APHA 4500SD	3.0	1.0	1.3
PH	ASTM D1293	9.4	7.7	8.8

Table 02 Sour Water Stripping Train02 Analysis

Feed Sour Water TR02	Method	Max. ppm	Min. ppm	Average ppm
NH3	UOP 740	6095.0	2192.0	4451.9
H2S	APHA 4500SD	9985.0	5900.0	8810.1
Oil Content	ASTM D7066	10000.0	1000.0	3129.0
Product Stripped Water TR02	Method	Max. ppm	Min. ppm	Average ppm
NH3 (50 max.)	UOP 740	31.0	15.0	24.9
H2S (10 max.)	APHA 4500SD	3.0	1.0	1.5
PH	ASTM D1293	9.4	7.0	8.1

Table 03 Chlorides concentration in the treated sour water

Product Treated Water		Max.	Min.	Average
Chlorides	UOP 456 ppm	14	6	9
		17	8	12
		10	5	8
		33	9	20
		16	6	11
		23	7	15
		16	6	10
		16	5	10
		25	5	12
		10	4	7

Table 04 Phenols concentration in the treated sour water

Sample (feed /product)		In Wash Water	Out in Brine water
Phenols	ASTM D 1783 ppm	48	26
		38	17
		39	17
		21	11
		17	11
		16	10

For table 03/04 represents the amount of chlorides that can be present in the treated water that can limit the use of treated stripped water in reference to the use and presence of stainless steel material in process units, the chlorides content needs to be in eliminated or limited to avoid chloride attack.

4. DISCUSSION:

The section provides the analysis of the results and their implications for the petroleum refining industry and represents the environmental benefits and the economic study evaluation.

- ### ENVIRONMENTAL BENEFITS:

Table 01/02 represents the result for the analysis done for feed sour water and treated product stripped water. NH_3, H_2S, Phenol and Chlorides content in treated stripped water, it is worth mentioning that the SWS Unit treatment results represented with a higher efficiency for the contaminants removal that is done in most of the refineries , as this environmental units gained recently a higher importance in order decrease and control contaminants like GHG, SO_X , NO_X and Phenol . These units are considered responsible for the treatments needed and also dispose the contaminants to the safe location. The only part that needs to be clarified that the performance of the unit and the treatment analysis is the bottle-neck for water reuse in any industrial application .

According to the analysis done for both NH_3 and H_2S max average results for the product stripped water was 25, 1.5 ppm respectively and the chlorides result was 20 ppm. The limit of chloride inorder reuse as an air cooler wash water is 100 ppmw max. and the recommended value is 5 ppmw according to (API Recommended Practice 932-B, JUNE 2019)[8] (as represented below in Table 05). The clean condensate analysis results is nil for chlorides, ammonia and hydrogen sulfide.

Phenol amount also varies depending on the olefins present in the intermediate products that is going to be treated and produce sour water that contains high Phenol content example: thermal cracking units that can produce Olefins like Coker Units. The phenol is produced from a dedicated train a directed towards the deslater for phenol recovery as mentioned before.

Table 05 Quality parameters of injected wash water

Parameter	Maximum	Desirable Target
Oxygen (ppbw)	50	15
pH	9.5	7.0 to 9.0
Total hardness (ppmw as Ca hardness)	2	< 1
Dissolved ion (ppmw)	1	0.1
Chlorides (ppmw)	100 [a]	5
H_2S (ppmw)	—	< 1000 [b]
NH_3 (ppmw)	—	< 1000 [b]
Total suspended solids (ppm)	0.2	Nil

[a] While chloride levels up to 1000 ppm in NH_4HS solutions have shown no apparent increase in carbon steel corrosion, chlorides should be kept to 100 ppm or less due to the potential for stress corrosion cracking of any 300-series stainless steel in the downstream sections of the hydroprocessing unit.

[b] Target and maximum concentrations are system-specific as H_2S and NH_3 are additive to the process stream concentrations.

Water management is a crucial element of sustainable production in the petroleum refining industry. The purpose of water regulatory activities is to ensure water source conservation, enforce environmental standards, and encourage permanent change. The following are the main elements of water-related regulation (Water discharge threshold) which is represented in table 06/07 in reference to the Egyptian Laws 48/82 and amendment 92/2013 . Regulatory bodies set the maximum allowable levels for various wastewater discharges into the receiving water bodies. These standards normally include pH, temperature, oil and grease, total suspended solids , chemical oxygen demand , biological oxygen levels, and individual pollutants and heavy metals as represented below.

The guidelines indicate the highest tolerable concentration of pollutants in refinery wastewater. The tolerable limits vary depending on the process type and the ecological soundness of the receiving water . Adhering to the guidelines is vital to the quality of water and maintaining the soundness of the ecosystem. Water Conservation requirement frameworks are increasingly concerned with the possibilities of water scarcity. As a result, refineries are mandated or encouraged to adopt water reuse and recycling, process optimization .

This process optimization and treatment to reach less than the threshold limits should be implemented from the source of individual effluent units either by treatment or dilution

Table 06 waste water discharge threshold part 01

Pollutant	Threshold
Cyanides	0.1 ppm
Flourides	0.5 ppm
Phenols	0.05 ppm
Mercury	0.01 ppm
Lead	0.1 ppm
Cadmium	0.003 ppm
Arsenic	0.05 ppm
Selenium	0.1 ppm
Chromium total	0.1 ppm
Copper	0.5 ppm
Nickel	0.5 ppm
Zinc	2 ppm
Iron	1 ppm

Table 07 waste water discharge threshold part 02

Pollutant	Threshold
Delta T	3°C Max
Total Suspended Solids (TSS)	50 ppm
TDS	2000 ppm
P/PO4	10 ppm
NH3	3 ppm
NO_3^-	40 ppm
NO_2^-	40 ppm
COD	80 ppm
BOD5	60 ppm
pH	6-9
Oil and Grease	10 ppm
Turbidity	50 NTU
Sulphide	1 ppm
Dissolved Oxygen	4 ppm

- **ECONOMICAL EVALUATION:**

Using the clean condensate 100% quantity is considered the perfect and the safest source for use but costly more expensive, finding another source for wash water that achieves the specification mentioned before will be an advantage environmentally and economically. The use of Produced Stripped water (treated water) in a mix with Condensate in a percent of 50/50% (Abdulaziz Alzanan, 2022) [9] as a wash water for the REAC, the reference for reuse is the chlorides content in the mix which based on the analysis that can be reached if exceeded or decreased, by adjusting the ratio of mix day by day.

The total treated water used in our case was 28 m3/hr instead of Clean Condensate and it can be calculated on a reference of Demi water /BFW/Chemical treatment used in-order give the opportunity to be used again for the production of steam.

Wash water from Clean Condensate header solely for the 100% condensate use as wash water which is 56 m^3/hr, will have an operating cost (Opex.) of about 2,352,000$/year. While in case we kept condensate utilization with 50% (28 m^3/hr) the Refiner will have cut down in operating cost with (28 m^3/hr*8400 hr * 5 $/$m^3$ = 1176000 $/year). Also using this philosophy will give an advantage and a surplus amount of Dematerialized/Condensate water Unit with 28 m^3/hr, which will decrease the load on Demi unit significantly.

Notes:

- The 28 m^3/hr is equal to the 50% of wash water needed for UOP Units.
- 5 $/$m^3$ is taken as the Dematerialized Water costs ,and the treatment cost for condensate is higher due to chemicals added to the condensate recovered during BFW treatment .
- Also the use of condensate is preferred rather than Dematerialized Water due to its high temperature.
- Raw water for industrial applications cost increased from 0.1622 $/ m^3 in 1998 and increased to 0.85 $/$m^3$ in 2016 and suspected to be increased in the upcoming years.

5. CONCLUSION:

Based on the study, it can be concluded that using refinery treated sour water as a sustainable water management practice in the petroleum refining industry is not only feasible but also provide a huge advantage. The study found that the treated sour water met the water quality standards for reuse, and it could be used for various purposes such as REAC Wash Water and Brine crude washing feed water. Additionally, the use of treated sour water reduced the demand for freshwater, which is a scarce resource in many regions.

The importance of using treated sour water as a sustainable water management practice cannot be overstated. The petroleum refining industry is a major consumer of water and generates large volumes of wastewater, which can have harmful impacts on the environment if not properly treated. By treating and reusing sour water, refineries can reduce their water consumption, minimize their environmental footprint, and contribute to the conservation of freshwater resources.

In **conclusion**, the use of refinery treated sour water as a sustainable water management practice is a win-win solution for the petroleum refining industry. It not only reduces the demand for freshwater but also minimizes the environmental impact of the industry's operations. Therefore, it is recommended that refineries consider implementing this practice as part of their sustainable water management strategy.

6. RECOMMENDATIONS:

Future research should focus on providing a huge potential on further treatment of all waste water effluents depending on the specs of all individuals from zero cost treatment (direct use) like the use of stripped water to the costly one, by providing the needed treatment to achieve a clean water that can be used for BFW, DEMI and cooling water or even irrigation water. to reach zero discharge towards the waste water treatment (WWT), this can be achieved by a use of Ultra filtration Membrane that will give the treated water further treatment and will allow more decrease in NH_3, H_2S, Phenol that can restrict in some cases the reuse of the treated water as in case of using it as a makeup for cooling water due to the presence of sulfur reducing bacteria (SRB).

In general Water Reuse and Recycling within refineries by conducting studies and analysis on the quality of waste water effluents and finding the cure for each source is the supplement for water conservation and complete water management philosophy.

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