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Plant Modification to Re-Use the Produced water from the De-Hydration Unit in NGL Plant in Irrigation

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ABSTRACT: Simple modification of NGL plant process flow to treat the produced water in Oil and Gas industry. If produced water meets appropriate water quality criteria, it may be used beneficially for purposes such as irrigation, livestock watering, aquifer storage, stream flow augmentation, and municipal and industrial uses. Treatment may be required to improve the quality of produced water so that it can be put to beneficial use as in our paper as the produced water was injected to the Sewage Treatment Unit with different ratios to digest the Oil and Glycols by the Microorganisms using additional Nutrient, Continual monitoring for oil content and the glycols concentration using oil in water instrument and gas chromatograph to monitor the progress to know the optimum injection rate of the produced water to the Sewage Treatment unit which was 100:900 respectively.

KEYWORDS: De- Hydration, Gas, Irrigation, NGL, Produced Water

I. INTRODUCTION

Produced water is defined as the water that exists in subsurface formations and is brought to the surface during oil and gas production. Water is generated from conventional oil and gas production, as well as the production of unconventional sources such as coal bed methane, tight sands, and gas shale. The concentration of constituents and the volume of produced water differ dramatically depending on the type and location of the petroleum product. Produced water accounts for the largest waste stream volume associated with oil and gas production.

Petroleum Resource Formation and Production Conventional Oil and Gas

Oil is formed from plant and animal material that accumulates at the bottom of a water supply such as an ocean, river, lake, or coral reef. Over time, this material is buried by accumulating sediment and is pushed deeper into the earth's surface where the pressure increases from the weight of the overlying sediment and the temperature increases due to heat from the earth's core. Oil and gas reservoirs are created when hydrocarbon pyrolysis occurs in a confined layer of porous reservoir material. The confined material restrains the fossil fuel in the subsurface, while the permeable and porous reservoir material allows for accumulation. Oil exists underground as small droplets trapped inside the small void spaces in rock. When a well is drilled into an oil reservoir, the high pressure that exists in the reservoir pushes oil out of the small voids and to the surface [1].



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Unconventional Petroleum Resources

Oil shale, gas shale, tight sands, and coal bed methane are considered unconventional petroleum resources. Oil shale reservoirs are confined in sedimentary formations. Oil shale formations do not convert hydrocarbons into crude oil. Oil shale commonly is refined to produce a cleaner energy product for high grade fuel use. Tight sedimentary formations retain the hydrocarbons requiring energy and water intensive well development. Fracturing polymers in combination with water are injected at high pressures into the reservoir formation. Fracturing is necessary to produce sufficient effective aquifer conductivity to allow the production of economical quantities of oil and gas. The United States has the largest oil shale deposits. The Green River formation in Wyoming, Colorado, and Utah contains the largest oil shale deposit in the United States. Seventy percent of the commercially attractive resource in the Green River formation resides on land managed by the United States Federal Government.

Water produced during oil and gas extraction operations constitutes the industry's most important waste stream on the basis of volume. The oil and gas industry produces approximately 14 billion bbls of water annually [2]. The water varies greatly in quality and quantity and in some cases the water can be a useful by-product or even a salable commodity. Produced water is most often considered a waste, but the industry is beginning to consider this material as a potential profit stream. Whether waste or commodity, produced water has management costs that need to be kept inline with each specific production project and region or it could adversely affect the life of the well, thereby leaving substantial recoverable reserves in the ground. Produced water handling practices must also be environmentally protective or the operator could face regulatory action. Produced water handling methodology depends on the composition of produced water, location, quantity and the availability of resources [3].

Some of the options available to the oil and gas operator for managing produced water might include the following:

- 1. Avoid production of water onto the surface Using polymer gels that block water contributing fissures or fractures or down hole Water Separators which separate water from oil or gas streams down hole and re-inject it into suitable formations. This option eliminates waste water and is one of the more elegant solutions, but is not always possible.
- 2. Inject produced water Inject the produced water into the same formation or another suitable formation; involves transportation of produced water from the producing to the injection site. Treatment of the injectate to reduce fouling and scaling agents and bacteria might be necessary. While waste water is generated in this option, the waste is emplaced back underground.
- 3. Discharge produced water Treat the produced water to meet onshore or offshore discharge regulations. In some cases the treatment of produced water might not be necessary.
- 4. Reuse in oil and gas operations Treat the produced water to meet the quality required to use it for drilling, stimulation, and work over operations.
- 5. Consume in beneficial use In some cases, significant treatment of produced water is required to meet the quality required for beneficial uses such as irrigation, rangeland restoration, cattle and animal consumption, and drinking water for private use or in public water systems [4-9].

II. MATERIALS AND METHODOLOGY

The reuse of effluent by irrigation can make a significant contribution to the integrated management of our water resources. So in our research in Egypt NGL in Port Said we focused to utilize the produced water in the Irrigation after remove the main harmful parameters such as Methanol, Glycol and stable oil in water by Biodegradation of the simple aliphatic chain and the oxygenated Hydrocarbon by the Microorganisms in the Sewage Treatment Unit and then we can use the outlet effluent in irrigation.

Bench Top trial have been done with different ratios of the produced water which coming out from the De-Hydration Beds which contain active molecular sieve to remove the water from the gas before the fractionation process with different ratios of the Sewage water from the Aerator tank from the Sewage Treatment Unit with air supply to keep the microorganisms alive.



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The Oil content was easily degraded by the microorganisms but the Oxygenated compounds required additional of Urea as Nutrient source to the microorganisms.

NGL Plant in Egypt has 5 dehydration beds for water removal from the inlet gas stream which contains different sizes of Molecular Sieve for water and glycol removal, the processed gas distributed through 4 dehydration beds while the fifth one in regeneration process by passing hot gas to remove all the water and the accumulated methanol & Glycol to be disposed in the oily water sump to be treated through oily water system to remove the oil from the water before dispatch the water to another company for disposal. The current Oily water treating unit (API Gravity Separator) outlet minimum specification is 1000 mg/l of oily water by gravimetric technique and it is not able to remove the glycols and the injected methanol due to the miscibility of them in the water.

The idea to transfer the oily water outlet of the oily water unit to the sewage tank to be used later in the irrigation started to calculate the dosage rate and the ability of the sludge to digest the oil as normal hydrocarbon and also the glycols. Bench top simulation process done using the live sludge with instrument air as aerator which from the STP unit (Sewage Treatment Unit) to keep the sludge alive.

Oil in water concentration was monitored by Horiba OCMA-350 Oil Content Analyzer using S316 (dimer/ trimer of chlorotrifluoroethylene) extraction solvent.

We have Used S-316 solvent to quantitatively determine the oil content in the extracted sample. The oil / solvent solution is then simply transferred to the OCMA-350 analyzer for single-button measurement. Analysis is based on infrared (IR) spectral data, with peak integration (at approximately 3.4 μ m) to determine oil concentration. S-316 solvent is non-absorbent at this IR wavelength, so only oil is measured. Accurately measures oil down to 0.01 mg/l.

The extraction procedure done using 1:1 from the effluent sample and the S-316 in Separating Funnel all of the oil that present in the water will be extracted in the S-136 and will be in the bottom layer due to the density difference.

Pure S-316 will be used as blank and then the concentration of the extractable oil will be determined. The used S-316 can be re-used after reclamation using activated charcoal and silicon treated filter papers in three layers and we can confirm the oil removal by measuring the outlet S-316 as unknown sample.

Different trials done with different ratios of the sludgy water and the disposal water to find the optimum ratios and time of the settling to enable the micro-organisms to digest the oil and glycols to have water in quality to be used for irrigation.

Continuous monitoring of the oil in water of the feed water to the STP unit by Horiba OCMA-350 Oil Content Analyzer and also determining the glycol and methanol concentration was monitored by Varian 3800 Gas Chromatography the calibration of the Glycol shown in figures (1 & 2).

GC calibration conducted using different concentration De-Ionized water and fresh Glycol that used in the field to reduce the hydrate process in the gas producing process

The first trial was done with 5 different ratios between the disposal water which contain 2260 mg/l of oil in water, 1.5 Wt % methanol and 2.2 Wt% of Di-Ethylene Glycol.

The trials done for 5 days and the results are shown in Table (1) for Oil in Water Concentration, Table (2) for Methanol concentration and Table (3) for Di-Ethylene Glycol.

III. EXPERIMENTAL RESULTS

Table 1: Oil Content in the Disposal water in different ratios for 5 days

Disposal Water/ Sludge	Oil Content in Water mg/l					
water (ml)	Day 1	Day 2	Day 3	Day 4	Day 5	
750:250	1570	1100	570	110	20	
500:500	1220	760	205	95	18	
250:750	1170	625	165	71	18	
150:850	620	210	92	25	10	
100:900	410	121	52	10	5	

* The initial concentration of the Oil content was 2262 mg/l



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The above table shows the degradation of the oil which in the outlet water by increasing the volume of the Sludge which make the last ratio is the best one after five days.

Disposal Water	Methanol Content in Water Wt%					
/ Sludge (ml)	Day 1	Day 2	Day 3	Day 4	Day 5	
750:250	1.5	1.4	1.2	1.0	0.8	
500:500	1.5	1.3	1.2	1.0	0.8	
250:750	1.5	1.2	1.1	0.9	0.7	
150:850	1.5	1.1	0.8	0.8	0.7	
100:900	1.5	1.1	0.8	0.7	0.6	

Table 2: Methanol Content in the Disposal water in different ratios for 5 days

* The initial concentration of methanol content was 1.5 Wt%.

The microorganisms reduced the methanol concentration but not as much as needed to re-use the water for irrigation.

Table 5. Orycor Content in the Disposal water in different fattos for 5 days						
Disposal Water	Di-Ethylene Glycol Content in Water Wt%					
/ Sludge (ml)	Day 1	Day 2	Day 3	Day 4	Day 5	
750:250	2.2	2.2	2.2	2.2	2.1	
500:500	2.2	2.2	2.2	2.1	2.0	
250:750	2.2	2.12	2.11	2.0	2.0	
150:850	2.2	2.0	1.98	1.98	1.7	
100:900	2.2	1.90	1.75	1.70	1.52	

Table 3: Glycol Content in the Disposal water in different ratios for 5 days

* The initial concentration of methanol content was 2.2 Wt%

The microorganisms couldn't digest the oxygenated hydrocarbon even by increasing the ratio such as 100:900 disposal water / Sludge after 5 days so it need nutrient addition to complete the digestion process.

Table 4: 0	Dil Content in the Disposal water in different ratios for 5 days with 10% Urea Addition
ol Watar	Oil Contant in Water mg/l

Disposal Water	Oil Content in Water mg/l					
/ Sludge (ml)	Day 1	Day 2	Day 3	Day 4	Day 5	
750:250	1570	1000	420	100	10	
500:500	1110	660	120	55	5	
250:750	925	498	92	42	5	
150:850	780	326	72	23	2	
100:900	590	110	61	32	2	

* The initial concentration of the Oil content was 2281 mg/l

Addition of urea didn't change much the results because the presence hydrocarbon is not complicated to be digested but it gave better final concentration of the oil content for the effluent water.



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Table 5: Methanol Content in the Disposal water in different ratios for 5 days with 10% Urea Addition							
Disposal Water	Methanol Content in Water Wt%						
/ Sludge (ml)	Day 1	Day 1 Day 2 Day 3 Day 4 Day					
750:250	1.6	1.1	0.5	0.2	0.1		
500:500	1.4	0.8	0.5	0.4	0.3		
250:750	1.4	0.7	0.6	0.5	0.3		
150:850	1.3	0.65	0.5	0.3	0.3		
100:900	1.1	0.5	0.1	0.05	<0.001		

* The initial concentration of methanol content was 1.6 Wt%

Urea addition make the microorganisms stronger to digest the glycols up to <0.001 in the last ratio after five days.

Disposal Water	Di-Ethylene Glycol Content in Water Wt%						
/ Sludge (ml)	Day 1 Day 2 Day 3 Day 4 Da						
750:250	2.2	1.9	1.7	1.6	1.4		
500:500	2.2	1.9	1.6	1.2	1.0		
250:750	1.8	1.5	1.1	0.9	0.6		
150:850	1.5	1.1	0.8	0.5	0.4		
100:900	1.0	0.6	0.2	0.05	< 0.002		

Table 6. Glycol Content in the Disposal water in different ratios for 5 days with 10% Urea Addition.

* The initial concentration of methanol content was 2.2 Wt%

Urea addition make the microorganisms stronger to digest the methanol and reduced the concentration up to the <0.002 in the last ratio.

Figure 1: Three Level Calibration Curve of the Di-Ethylene Glycol in Distilled Water

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The above calibration figure shows the linearity of the curve and the accuracy of the prepared standards to produce accurate results to support the research.

Figure 2: The Peak Areas of the Three Concentration of the Di-Ethylene Glycol Used for the Calibration

	BY MFA EQ Figure.2 The Peak Areas of the Three Concentration of the Di-Ethylene					
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The peak area shows the instrument sensitivity and the column repeatability without any peak shifting on the base line and also showing the purity of the used standards beside the correlation between the standard concentration and the peak area.

IV. DISCUSSION

The first trials without adding Nutrient in Tables (1,2 &3) showed good degradation of the oil content because it is almost short aliphatic chained hydrocarbon but the sludge faced difficulties to digest the Oxygenated compounds such as the Methanol and the Glycols as it need to be stronger to reduce the glycols to easier form then to digest it. Adding nutrient to the sludge to be stronger such as Urea helps to enhance the glycol digestion in the STP unit.

The addition of the Nutrient was conducted in the Lab by quantities as 1%, 2% up to 10% of Urea.

Urea was used for Nitrogen source as nutrient for the sludge and the PH was optimized by adding sodium Hypochlorite to maintain the PH up to 7.

By checking the same analysis on the outlet water good results obtained the good results of the outlet water obtained by 10% addition of the Urea to the sludge in the de-aerator tank.

The trials done for 5 days and the results are shown in Table (4) for Oil in Water Concentration, Table (5) for Methanol concentration and Table (6) for Di-Ethylene Glycol.

V. CONCLUSION

We can use the produced water after injecting it in the Sewage treatment unit for irrigation by injecting it to the Oily Water accumulation sump by 1:9 ratio daily with addition of 10 % of Urea to the Aeration tank in the Sewage Treatment Unit and perform regular check to the outlet water for the additional parameters such as Glyco, Methanol and oil content beside the regular parameters such as P, Color and the residual chlorine. We manage to install stroke pump to inject the produced water into the sewage treatment unit sump by one Liter Litter per hour.



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References

[1] Taulis, M.E. Australia and New Zealand CBNG development and environmental implications. In Coalbed Natural Gas: Energy and Environment; Reddy, K.J., Ed.; Nova Science Publishers:; pp. 401–424, New York, NY, USA, (2010).

[2] McGraw-Hill AWWA. Water Treatment Plant Design. New York, G.P. Fulton, Water Treatment Plant Design. American Water Works Association (AWWA) and American Society of Civil Engineers (ASCE) (New York: McGraw-Hill (2005).

[3] Ayers, R.S., and D.W. Westcot. 1994. "Water quality for agriculture." Food and Agriculture Organization Irrigation and Drainage Paper, 29, Rev. 1, (1994).

[4] Reynolds Rodney R.: "Produced Water and Associated Issues," a manual for independent operator, Petroleum Technology Transfer Council, Vol. 6, pp. 23-26, (2003).

[5] Veil J.A., Puder M.G., Elcock D., and Redweik R. Jr. J.: "A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane," W-31-109-Eng-38, US DOE (January 2004).

[6] Broussard P. "Skip" Jr.: "Floatation Pump Proves Successful for The Treatment of Produced Water," paper presented at the 10th IPEC, pp 51 (2003).

[7] Design Guide for the Disposal of Wastewaters by Land Application; WP-7 Water Conservation by Reuse (SPCC 1986).

[8] APHA 1998, Standard Methods for the Examination of Water and Wastewater. American Public Health Association, 19th edition, Washington, DC. ARMCANZ and ANZECC 1995, National Water Quality Management Strategy: Guidelines for Groundwater Protection in Australia, Australia (1995, 1998).

[9] ANZECC (Australian and New Zealand Environment and Conservation Council) and ARMCANZ (Agriculture and Resource Management Council of Australia and New Zealand). Australian and New Zealand guidelines for fresh and marine water quality, Aquatic Ecosytems (Chapter 8) Volume 2, pp. 4, (2000b).