

# REDUCTION OF POLLUTANT TOXICITY LEVELS IN PRODUCED WATER FROM CRUDE OIL PRODUCTION PROCESSES

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## Abstract:

Produced water from crude oil production process is imbued with various contaminants which makes it unsafe for discharge into the environment without adequate treatment. The weight fractions of these contaminants vary from one well to another depending on the nature of the well, its age and production conditions. The discharge of produced water is subject to treatment which is usually aimed at reducing the weight fraction of the polluting components to a level considered safe for the environment by the regulator. The cost of treatment of produced water is prohibitive and surges as the age of the well increases and the reservoir characteristics change. The concentration of these pollutants (Benzene, Toluene, Phenol, Ammonia etc) in produced water could be altered by adjusting the production variables of temperature, pressure, residence time and flowrate. This paper has presented the results of simulation using HYSYS 6.2 to show that combination of temperature and pressure could decrease the concentration of the selected pollutants in produced water. This outcome is very important in oil and gas production in meeting regulatory limits for discharge of produced water and in the reduction of the cost of treatment of produced water.

**Keywords:** Produced water, pollutants, toxicity, production process, crude oil, temperature, pressure.

## 1 Introduction

Produced water is water trapped in underground formation that is brought to the surface during oil and gas production (Hagstrom *et al.*, 2016). It is an inextricable part of the hydrocarbon recovery processes, yet it is by far the largest volume waste stream associated with hydrocarbon recovery. (Dal Ferro and Smith, 2007). Produced water could be a weakly acidic solution with high content of chloride ions and mixture of calcium, sodium, potassium, magnesium salt solution which are highly corrosive because of high content of calcium and magnesium chlorides (Turkayeva *et al.*, 2017). Produced water contains a wide variety of constituents such as organic and inorganic pollutants, suspended solids, and iron. It has also been found to contain benzene, toluene, ethyl benzene, xylene (BTEX), polycyclic aromatic hydrocarbon (PAH), cobalt, nitrite, total nitrogen, sulfate, phosphate, zinc, phenols, arsenic, cadmium, chromium, barium, copper, iron, nickel, lead, vanadium with total petroleum hydrocarbon (TPH). These hydrocarbon and heavy metals have affected the composition of the seawater and sediments in offshore locations where they are discharged during crude oil and natural gas production operations (Okogbue *et al.*, 2017). The weight fractions of the pollutants found in produced water vary from one oil production well to another and depends on the nature of the well, its age and production conditions (Igwe *et al.*, 2013). Furthermore, injected water following produced water can bring traces of added chemicals such as biocides, corrosion inhibitors, scale inhibitors, emulsion breakers, coagulants / flocculants and oxygen scavengers to the surface (Johnsen *et al.*, 2004; Neff, 2002). These chemical constituents present in produced water, individually or collectively, could have significant impact on the environment. The large discharge volume, the complex content of particular hazardous chemicals and the lack of knowledge on possible long-term ecological impact has made produced water discharges the strongest target for concern and research in recent years (Bakke *et al.*, 2013).

Increasingly stringent environmental regulations require extensive treatment of produced water from oil and gas productions before discharge; hence the treatment and disposal of such volumes costs the industry annually more than USD 40 billion (Dal Ferro and Smith, 2007). Currently, properly treated produced water can be recycled and used for waterflooding [produced water re-injection (PWRI)] and other applications, such as crop irrigation, wildlife and livestock consumption, aquaculture and hydroponic vegetable culture, industrial processes, dust control, vehicle and equipment washing, power generation, and fire control (Veil *et al.*, 2004). These beneficial reuses directly decrease the withdrawal of potable water, a highly valuable commodity in many regions of the world. Although produced water can potentially be treated to drinking water quality (Tao *et al.*, 1993), little research has been done on the feasibility and cost-effectiveness of direct or indirect potable reuse of produced water from oil and gas production.

Monocyclic aromatic hydrocarbons (BTEX: benzene, toluene, ethyl benzene, xylene), polycyclic aromatic hydrocarbons (PAH) and related heterocyclic aromatic compounds are considered major toxicants in produced water (Neff *et al.*, 2011). BTEX are rarely included when considering the effects of produced water since they evaporate rapidly from seawater (Neff, 2002; Neff *et al.*, 2011; Terens and Tait, 1996). However, for organisms in close contact with discharge points, one cannot exclude subtle biological effects caused by chronic exposure to BTEX over a long period. PAH, on the other hand, constitute a diverse class of hydrophobic substances that are ubiquitous environmental contaminants (Harvey, 1997). Some PAHs are known to be potent carcinogens and this class of contaminants is therefore given high priority for environmental pollution regulation and in risk assessment of industrial discharges. PAH may cause DNA damage (Aas *et al.*, 2000), oxidative stress (Sturve *et al.*, 2006), cardiac function defects (Incardona *et al.*, 2004) or embryotoxicity (Carls *et al.*, 2008). Alkyl phenols (AP) have created the greatest concern due to their documented hormone disrupting effects (Arukwe *et al.*, 2000; Nimrod and Benson, 1996; Soto *et al.*, 1991). Phenol and AP are both hazardous and can cause a range of biological effects (Priatna *et al.*, 1994). Naphtenic acids, another constituent of produced water, have been reported to function as xeno-estrogens (Thomas *et al.*, 2009). Metals in produced water include arsenic, cadmium, copper, chromium, lead, mercury nickel, zinc, barium and iron. Barium and iron are redox-sensitive and may precipitate as barium sulphate and iron as iron oxides / hydroxides. These processes may also influence the behavior of other metals e.g by co-precipitation (Azetsu-Scott *et al.*, 2007). The most abundant NORM element in produced water are radium-226 and radium-228.

There have been earlier attempts to reduce pollutant toxicity from produced water using adsorption by activated carbon (Naas, 2010). Heavy metals like Cr, Cd, Co, Ni, Cu, Pb have also been successfully removed from produced water by apricot seed derived activated carbon at low pH conditions (Kobya, 2005). Filtration media have been used to achieve an optimum removal efficiency of total organic carbon from the produced water (Renou, 2008). Chemical treatment process of precipitation (Li, 2000) and biological processes using micro-organism like algae, fungi and bacteria (Rodney, 2003) have been used to reduce the toxicity of produced water.

## 2 Materials and Methods

### 2.1 Case Study Process Plant

The Izombe Flow Station (IFS), which is currently operated by Addax Petroleum Development Nigeria Limited, is an onshore crude oil and natural gas facility located Oil Mining Lease (OML) 124 in Izombe, Oguta Local Government Area of Imo State, Nigeria. The flow station, which was commissioned on 6 June 1975, is a complete self-sufficient facility containing Oil and Gas Production and Processing Systems: Oil Production Process; Gas Compression and Re-injection Systems; and Produced Water Re-injection Unit. IFS was originally designed to receive 37,000 barrels per day of well fluids from Izombe, Ossu and Jisike fields. The well fluids are separated into their three components: oil, gas and water; and each component is further processed for final disposition. Crude oil is processed for export, natural gas is compressed to be used as either fuel, lift gas or re-injection gas while produced water is prepared for disposal through injection to the available injection wells.

### 2.2 Input Data

Three samples of varying sizes were collected in the recommended containers at each point and preserved using the appropriate reagents. The sample points are the production manifold, the outlet of the line heater and the inlet of the water injection (WIJ) pump. The sample at the production manifold is aimed at obtaining the condition of the produced water on arrival at the flow station prior to treatment. The samples from the outlet of the line heater are expected to show the effect of heat on the pollutants while the last samples collected at the inlet of the water injection pump are expected to reveal the effect of further treatment on the pollutants concentrations prior to the disposal of the produced water into a selected reservoir. The table below shows the conditions under which the samples were collected.

Table 1: Sample Collection conditions

Points of Collection	Time of Collection	Point Pressure	Point Temperature
Production Manifold	14:25 hrs	48 psi	39 °C
Outlet of Line Heater	14:35 hrs	23 psi	52 °C
Inlet of Water Injection Pump	14:45 hrs	14.7 psi	37 °C

The collected samples were subjected to laboratory analysis to determine the concentrations of some selected pollutants in the samples. The results of the laboratory tests are tabulated below:

Table 2: Results of the laboratory tests on samples collected at various points

S/N	Sample Parameter	Analytical Method	Concentration at Manifold (mg/l)	Concentration at Line Heater (mg/l)	Concentration at WIJ Pump (mg/l)
1	pH	pH Meter	7.10	6.97	6.68
2	Benzene	GC (FID)	0.50	0.19	0.02
3	Toluene	GC (FID)	0.52	0.15	0.08
4	Phenol	HACH DR 3900	0.72	0.21	0.12
5	Lead	AAS (FLAME)	1.25	0.98	0.41
6	Chromium	AAS (FLAME)	89.37	80.79	67.42
7	Phosphate	HACH DR 3900	0.03	0.12	0.14
8	Ammonia	HACH DR 3900	10.65	7.90	5.50
9	TDS	TDS Meter	17,100	16,600	12,400
10	Chlorides	Titrimetry	6,000	5,500	5,200
11	Salinity	Titrimetry	9,900	8,665	7,175

### 2.3 Process Simulation:

Aspen Hysys 6.2 has been used for this simulation. The process engineering software provides extremely powerful approach to steady state modeling. Soave-Redlich-Kwong (SRK) was the base property package selected for the simulation. The pollutant compositions were expressed in mass fraction. Some of the pollutants including chromium, iron, copper, lead, phosphate, and zinc.

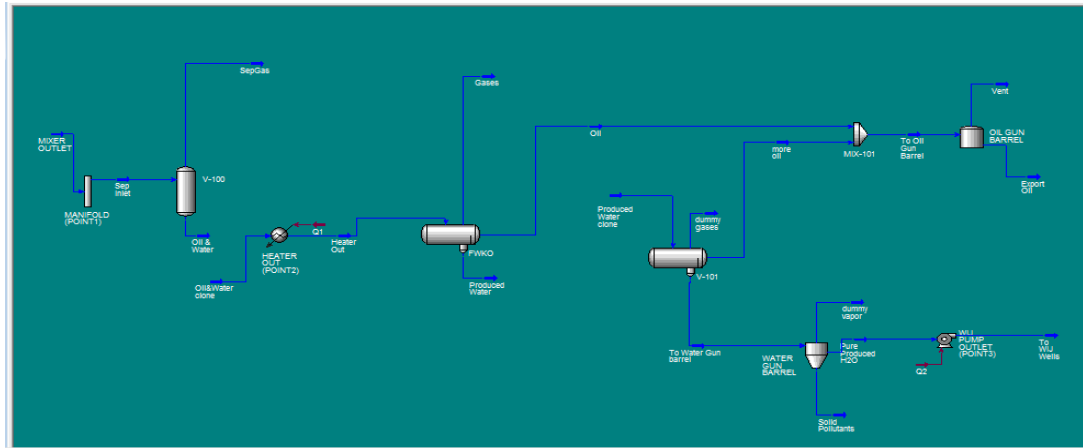
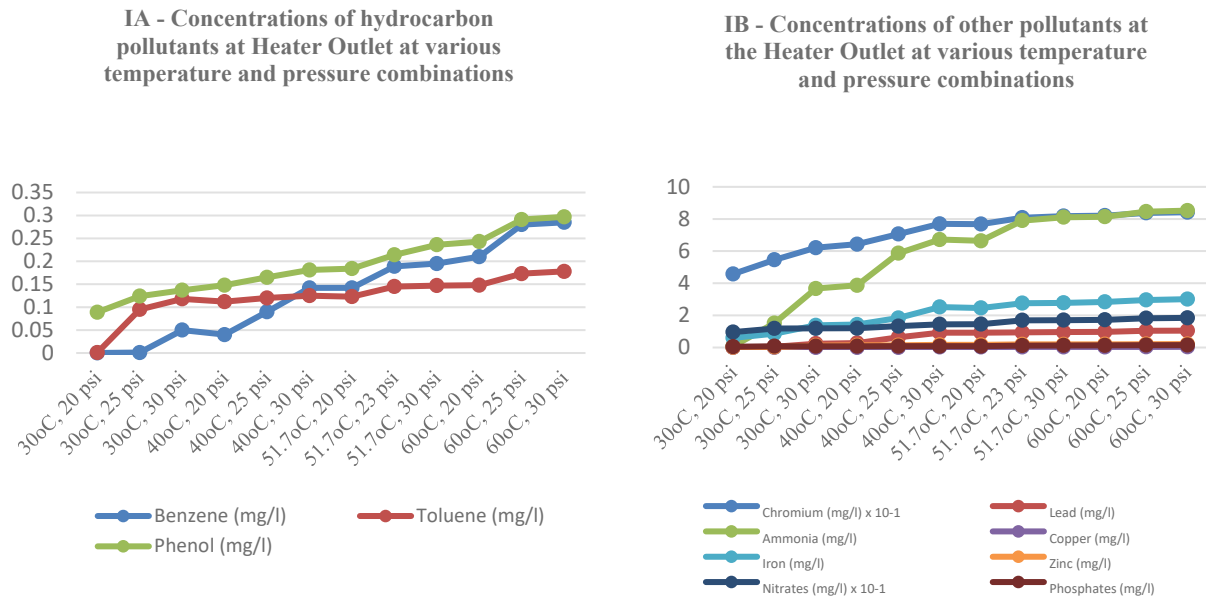


Figure 1: Process flow diagram of the facility showing the three sampling points

### 2.4 Toxicity Reduction Scenarios

The concentrations of the selected pollutants were observed as the pressure and temperature of the collection points along the production process were varied in a simulation environment. The simulation process had set the target of achieving produced water whose various pollutant concentrations are below the regulator's limit for disposal. The results of some the simulation are shown in the charts below:

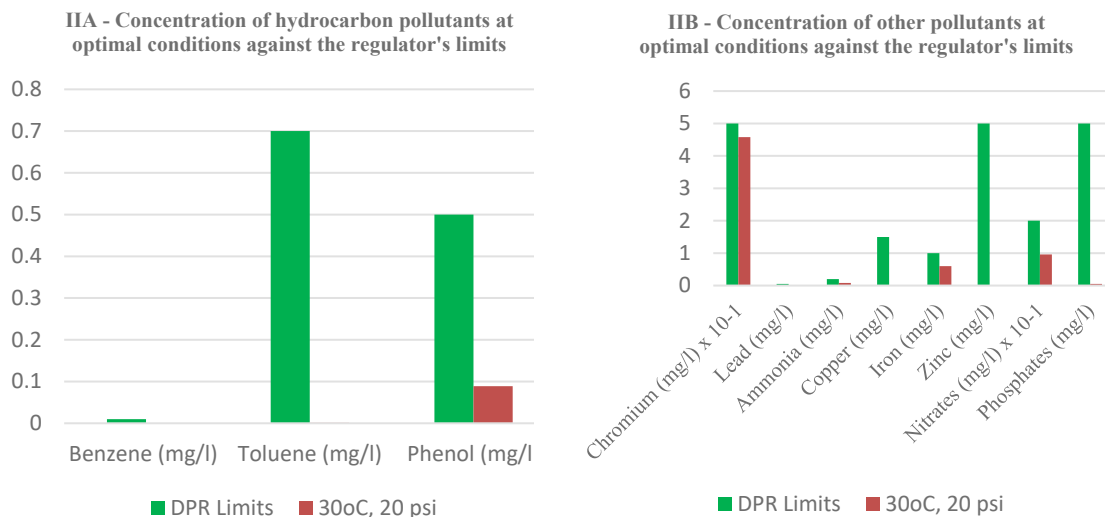
Chart I: Effect of temperature – pressure combination on the concentration of pollutants



### 3 Results and Discussion

The toxicity of a pollutant is directly proportional to the concentration of that pollutant in the produced water. The concentrations of the pollutants generally decreased along the production process from the manifold to the WIJ pumps. An increase in either temperature or pressure at any of the selected points on the production process showed increased in the concentration of pollutants but to different degrees. The results of the simulation process showed that the temperature of 30°C and pressure of 20 psi at the heater outlet is the optimal condition since it gave the best results which met the regulator's limits for all pollutants. Moreover, the Free Water Knock Out (FWKO) vessel which receives the fluid from the line heater can operate at these conditions.

Chart II: Concentrations of pollutants at optimum conditions against regulator's limits



### 4 Conclusions

Process simulation using Hysys 6.2 has been used to show that temperature and pressure variables could be used to reduce the toxicity of pollutants in produced water from crude oil production to meet the limits acceptable for disposal by the regulator. The results of the work suggest that there is an optimal point (temperature, pressure) at the which the pollutant toxicity is reduced to the minimum without incurring production losses. This result is required to save the cost involved in further treatment of produced water and thereby improves the cost per barrel of produced crude especially for ageing oil fields. The effect of other production variables like residence time and production chemicals on the toxicity of produced water could also be studied.

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