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Review paper

OVERVIEW OF PRODUCED WATER IN OILFIELD

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Abstract: Oil and gas reservoirs can contain water as a reservoir fluid. The water precentage ranges from a few (%) to almost total water saturation. The waters found in the oil and gas reservoirs are genetically related to oil origin and represent mixture of organic and inorganic materials. These waters are of marine origin and contain mineral salts such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3, SO_4. Produced water must be subjected to a particular treatment before the deposal so as not to contaminate the environment, primarly watercourses. The mineral composition of these waters can cause the occurence of limescale, which in turn result in damage of the equipment such as injection pumps, corrosion of metal parts etc. The paper presents an overview of the hydrochemical characteristics of the groundwaters of oil and gas reservoirs and produced water into the bargain. Produced or wastewater can be used among other things to inject into the aquifers of the oilfield to increase the production of crude oil as well as their treatment.

Keywords: produced water; chemical composition; water treatment;

1 INTRODUCTION

The production of oil and gas is often accompained with large quantity of produced water. There are estimation that wastewater production is three times larger than oil and gas product (Kusworo et al. 2018 and Dickhout et al. 2017). This ratio increases with the age of wells, so the amount of produced water is generated up to 7-10 barrels per day (Kusworo et al. 2018 and Zha et al. 2017). According to Pitchel (2016) the United States generates about 21 billion barrels of produced water every day. This water can pollute surface, groundwater and soil. There are various limits in different countries that produced water have to achieve. In Australia produced water discharge limit is 30 mg/l. On the other hand, based on the United States Environmental Protection Agency (USEPA) regulations, daily maximum limit for oil and grease is 42 mg/l and the monthly average is 29 mg/l (Fakhru'l-Razi et al. 2009).

Hydrogeological data have very important role in determination of the groundwater inflow source to the borehole. This water can penetrate both from exploitation layer and

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from other horizonts through the fractures zones or corrosion demage of the column, the non-hermetic pipe joint, etc. (Komatina, 1995).

2 CHARACTERISTICS OF GROUNDWATER IN OIL AND GAS RESERVOIRS

Affiliation of water is best determined by the chemical composition. Groundwater in traps of oil and gas reservoirs is usually very mineralized or brined. Factors such as geological location of the field, geological formation, lifetime of reservoirs affect the physical and chemical properties of produced water (Fakhru'l-Razi et al. 2009). Some authors such as (Pitchel , 2016) also mentioned hydrocarbon products as a factor of physico-chemical properties of water. Since the water comes in contact with the rocks of various compositions, it dissolves them to a bigger or smaller extent. Based on the amount of mineral matter that contains ground waters it can be distinquished by Komatina (1995):

1. fresh water, M< 1g/l,
2. mineralized water 4 g/l<M<10 g/l
4. very mineralized water 10g/l<M<50 g/l
5. salt brine M> 50 g/l.

Of organic matter, the most common are naphthenic and some fatty acid, and from gaseous substances methane hydrocarbons, CO_2 and H_2S. The presence of microcomponents J, Br, Li and NH_4 is also characteristic (Aksin, 1967). Negative values of oxidizing reduction potential (Eh), low value of the sulphate coefficient

$$\frac{SO_4 \cdot 100}{Cl} < 0.05$$

and the chlor-bromine coefficient

$$\frac{Cl}{Br} < 50$$

are used as indicators of favorable hydrogeochemical conditions of the hydrocarbons existence (Komatina, 1995).

3 PROBLEM OF LIMESCALE IN PRODUCED WATER

Most commonly produced water contains dissolved inorganic salts, organic components, gases, dispersed oil droplets, solid particles, as well as chemical aditives. (Prstojević, 2012).

In the system of preparation and disposal of produced water of oil boreholes, a special problem that occur is limescale:

$$Ca(HCO_3)_2 \rightarrow CO_2 + H_2O + CaCO_3$$
$$Ca^{2+} + CO_3^{\;2-} \rightarrow CaCO_3 \downarrow \qquad (1)$$

The tendency of the water for deposing $CaCO_3 \downarrow$ (1) determines the water stability that implies the ability of non-changing the composition during long contact with metal or concrete surfaces. Deposition of $CaCO_3$ can be represented by the saturation index (2) I_s where:

$$I_s = \log \frac{(C_{Ca})(C_{CO_3})}{K_{SP}} \qquad (2)$$

Where:

C - molar concentration of ions
K_{SP} - carbonate solution$CaCO_3$

Some measures to maintaun pipeline condition from external corrosion include anodic and carhodic protection, surface coating and position of pipeline above ground level. These measures reduce the opportunity for pipe leakage and oil spills (Marsid et al. 1994).

Due to the presence of the limescale, there is an accelerated consumption of injection pumps, the creation of local corrosive surface and the clogging of the filters In order to prevent the occurence of the limescale, design solutions must not allow the mixing of water with sulphates as well as maintenance of layer pressure, in order to prevent the separation of CO2 and carbon deposition (Prstojević, 2012).

4 COMPOSITION OF PRODUCED WATER

The production of crude oil also yields certain quantities of water considered as industrial waste. Separation of dispersed oil is the primary process of water treatment. The permitted quantities of dispersed oil vary from country to country, for example, in the USA concentration varies in the range of 15 to 58 mg (Danilovic et al. 2016).

The major compounds of produced water include: dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids (including formation solids, corrosion, bacteria, waxes and asphaltenes) and dissolved gaseous (Fakhru'l-Razi et al. 2009 ; Hansen et al. 1994). Concentration of salts in produced water are expressed as total dissolved solids (TDS) and the Total Oil Content (TOC). The value of TDS and TOC were were found in the range of 4000-50000 mg/l and 45-800 mg/l respectively (Kusworo et al. 2018). Dispersed and dissolved oil compounds in water contain mixture of hydrocarbons such as benzene, toluene, ethylbenzene, phenols, polyaromatic hydrocarbons, xylenes etc (Ekins et al. 2007). The amounts of these componets in produced water prior to treatment are related to factors such as: oil composition, pH, salanity, total dissolved solids, temperature, oil/water ratio, type and quantity of oilfield chemicals and type and quantity of various stability compounds (waxes, fine solids and asphaltenes) (Fakhru'l-Razi et al. 2009 and Hansen et al. 1994). Most of produced waters contain a wide range of dissolved organic and inorganic compounds, suspended solids such as sand and corrosion products and dispersed oil. The soluble inorganic constituents include both metals and non metals. Dispersed and soluble oil are always present in produced waters. The dispersed oil consists of a mixture of oil droplets from various sizes from less than 10 microns to more than 100 microns in diameter. The soluble oil are organic materials such as simple aliphatic and aromatic hydrocarbons, phenols, long chain fatty acid and napthenic acids. (Bansal et al. 1998). From the alkali and alkaline earth metals Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+} as well as Sr and Fe are present, usually in the form of chlorides, carbonates and hydrocarbonates. The anions are present in the form of Cl^-, SO_4, HCO_3. These cations and anions are affected water chemistry, salinity and scale potential (Fakhru'l-Razi et al. 2009 and Hansen et al. 1994). Sulfides occur in form of H_2S and Br_2S . In the form of colloids very often are detected Fe_2O_3, Al_2O_3 i SiO_2. Heavy metals such as mercury, lead, nickel, silver, chromium as well as metalloids in the form of arsenic in different concentration can be also found in oilfield produced water (Pitchel , 2016). Concentrations of these metals depending on age of the wells and formation geology (Fakhru'l-Razi et al. 2009).

5 TREATMENT OF PRODUCED WATER

There are three methods of produced water disposal: discharging into watercourses, injecting into aquifers and aquifers of oil reservoirs to increase the production of crude oil and gas.The waters are injected to maintain oil reservoir energy or increase oil and gas production must meet certain requirements in terms of quality. This water can not contain suspended particles neither organic nor inorganic, gassses which cause corrosion (CO_2, H_2S, O_2, Ba^{2+}, Ca^{2+}, Sr i Fe) in solution with sulphides, carbonates and microorganisms (iron sulphate-reducing and sludge bacteria). The presence of greasiness in water in the form of suspended particles with a diameter >0.45µm is detected (Prstojević, 1998).

Treatment of the waste oil water in a form of re-injection into geological formation was carried out on the Amal oil field in Lybia. This method was applied primarily to maintain pressure and possible increase oil recovery. From the environmental point of view water flooding is the the most acceptable method for dealing with produced water economically. The proposed solution supports the system of waste water disposal into brine storage pits, but with crucial difference in that the disposed water will no longer be environmental harmful. (Danilovic et al. 2016). On (Figure 1) it can be seen one example of cost-effective process for the preparation of produced water at the Amal oil field on the basis of existing solutions and studies. From the sedimentation tanks R-1, R-2 and R-3 produced water is pumped to storage tank R-4, where additional gravitational sedimentation is carried out, but with smaller volume of produced water. After the tank R-4 water is routed through a buffer tank to coalescing filter with a hydrophobic medium. Treatment of produced water is done in the separator, using hydrophobic filtration and gravitation sedimentation with a liquid hydrophobic coalescing medium. The treated water from coalescing filter with a hydrophobic filter medium passes through a buffer tank and than to pumps which re-inject it into the geological formation (Danilovic et al. 2016).

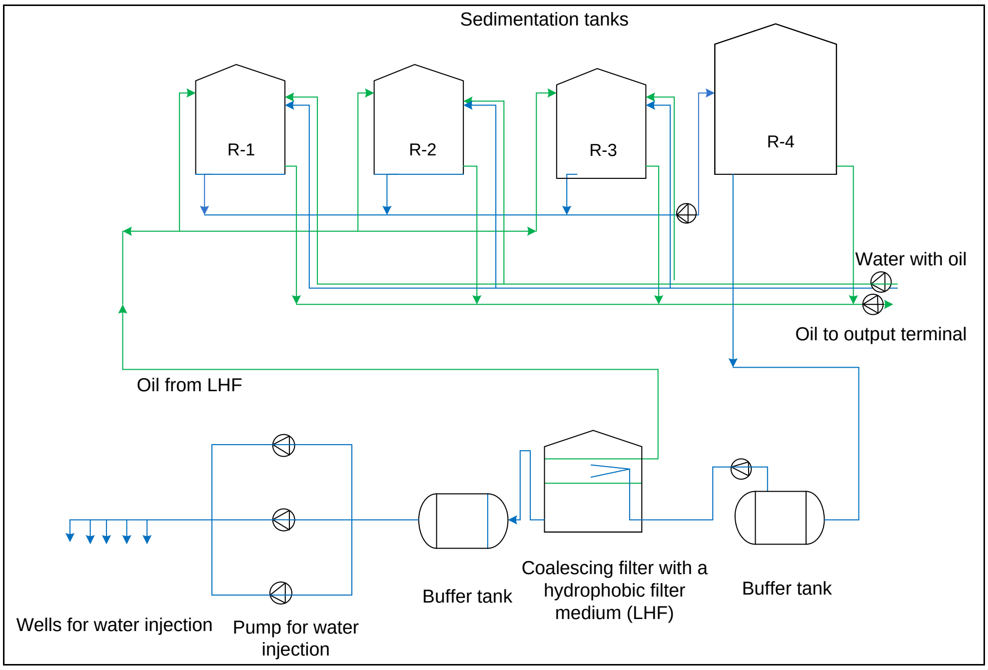

Figure 1 A scheme of preparation process of waste water (Danilovic et al. 2016)

Another operational system based on separation of oil, gas and water can be found at PT Caltex Pacific Indonesia oil field. PT Caltex Pacific Indonesia (CPI) is the local unit of Caltex which in October 2001 was renamed to Chevron Taxaco Asia. Separated water can be reused and return to the natural courses mostly through a canal system. This canal system would also enable easy access for oil recovery during emergency cases such as leakage and oil spills. Investigation shows that the wash tanks and double pit systems are sufficient to maintain oil content of produced water less then 25 ppm and temperature not higher than 45°C in order to protect the environment. From the chemical point of view, water range from fresh to slightly brackish depending upon the fields, with low content of chloride, alkalinity, salinity, hardness and conductivity. On the other hand, heavy metals have not been detected. On (Figure 2) oil collection system with separation oil from water and gas is shown (Marsid et al. 1994). Pump draws oil from the well and moves it initially through individual pipelines and than into common large bore field pipeline network system. The well fluid enters the Gathering Station where gas is separated at the gas boot. The recovery gas is than compressed at the gas compressor which removes water. Two wash tanks are used to separate the water leaving the oil for transmission to Dumai for shipping and sale. Leaving the pit system, the produced water is either reused or is returned to the natural water system. As the fields mature, more water is produced since the water cut increases and so it is necessary to continue to improve the pit system to maintain produced water quality.

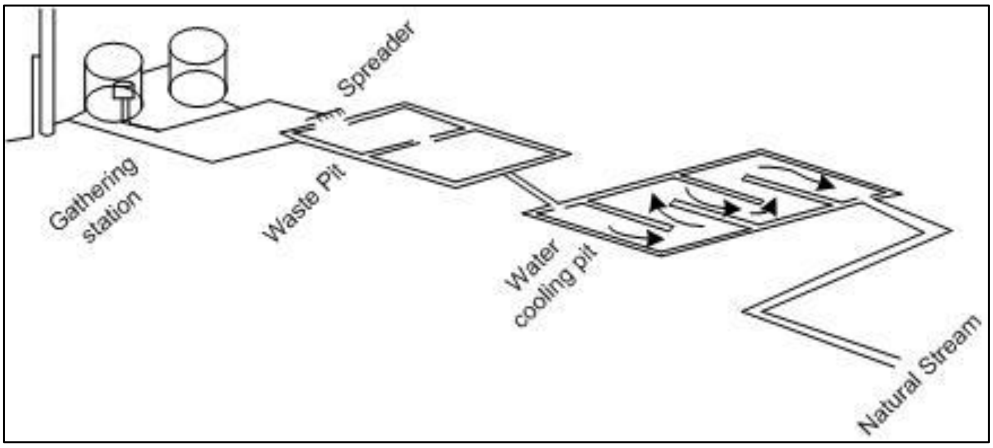

Figure 2 Scheme of the oil collection system and pit system for water treatment (Marsid M et al. 1994).

Also, another various methods of produced water treatment exist such as ozonolysis, biological methods, active sludge etc. Ozonolysis includes decomposing dissolved organic compounds. Sonochemical oxidation could destroy BTEX (mixture of benzene, toluene and the three xylene isomers). The experiment showed that during 3 days of exposure to ozone nearly all extractable organics could be destroyed. Zeolite membranes can also be applied. They possess stable chemical, mechanical and thermal properties.Treating oilfield-produced water with zeolite it can be achieved separation of various ions such as Na^+, K^+, Ca^{2+} and Mg^{2+} (Fakhru'l-Razi et al .2009 and Liu et al. 2007). Another method for produced water treatment is biological method. For this purpose aerobic and anaerobic microorganisms is used. For example, aerobic treatment includes active sludge, trickling filters, chemostate reactors, biological aerated filters and lagoons. Active sludge is the usual method for treating wastewater (Fakhru'l-Razi et al. 2009). Furhtermore, some authors proposed zirconia oxide ceramic membranes technology for removing suspended solids, oil and grease. The results showed that was possible to generate an effluent containing oil and grease with suspended solids lower than 5 mg/l. Under these conditions produced water becomes suitable for reinjection or adequate for use in subsequent desalination processes (Weschenfelder et al. 2015).

6 CONCLUSION

Mineral composition of ground water in oil and gas reservoirs is of great importance due to the chemical reaction with equipment such as injection pumps, drill pipe connections,etc. It was observed that corrosion of metal parts of drilling rig can also occur. The chemical composition of these waters depends on the petrological composition of the rocks through wich they flow, whereby we can distinguish more or less mineralized waters. The treatment of the produced water must be carried out before storing it, returning to watercourses or returning into the borehole. As one of the important problems of this water is the occurence of limescale. Changing the pressure and temperature of ground water when entering to the borehole leads to a sudden deposition of $CaCO_3\downarrow$ due to release of $CO_2\uparrow$ and decrease in pH, which can lead to clogging of the oil production layer. Consequently, special attention should be paid to the chemical composition of the ground waters in order to minimize these phenomena. Some of the methods of treating produced water in the world is their storage and processing in evaporation in brine storage pits so they can not contaminate natural environment primarly watercourses with sulfur compounds, heavy metals, phenols, microorganisms etc. On the other hand, great attention should be paid to the chemical composition as well as the methods of treatment of produced water such as ozonolysis, biological methods, active sludge etc, if they are returned again to the boreholes to increase the production of the oil.

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