Influence of Gamma Radiation on the Treatment of Sulfate Reducing Bacteria in the Injection Water Used for the Enhanced Oil Recovery

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Received: 8/6/2013 Accepted: 10/8/2013

ABSTRACT

The counts of sulfate reducing bacteria (SRB) in the water samples collected from the well head (formation water) and outlet of petroleum treatment plant (Produced water) in a petroleum field in middle delta- Egypt were determined. The data showed a low count of (SRB) in the collected formation water sample and there was an obvious increase in the bacterial counts which appeared in the produced water, that may reveal that the presence of appropriate conditions for the growth of (SRB) in the closed system in treatment plant. Two scale inhibitors were tested through jar test, the scale inhibitor I had maximum efficiency at 20 ppm, two SRB biocides were screened for their bactericidal activities. It was found that the biocide A was slightly superior in respect to the antibacterial efficacy compared to B in presence of 20 ppm scale inhibitor. These biocides were test for the study of the combined treatment with gamma radiation to maximize the efficiency on sulfate reducing bacteria using the minimum effective dose of both radiation and biocides to eliminate the negative impacts of the chemicals used and the radiation applied. The results demonstrated that, the lethal doses of biocides were (300 ppm) of biocide A or (400 ppm) of biocide B at 1kGy irradiation dose. The treated produced water was evaluated in respect of enhanced oil recovery, the data showed increase of the recovery capacity by the irradiation and chemical treatment. This technology could be used for the water that are injected into reservoirs, and suitable for oil field and pipeline operators, and presented a viable bacteria control method.

INTRODUCTION

Water injection is a common enhanced oil recovery (EOR) method, usually applied in offshore oil fields for the purpose of pressure maintenance and enhanced oil recovery. During secondary and tertiary recovery by this method, reductions of permeability have been observed in many reservoirs. Several sources are recognized as possibly contributing to this problem such as mineral scale deposition, solid invasion, clay swelling and rock-fluid incompatibility.

One of the most important and hazardous kinds of these phenomena is mineral scale deposition due to the incompatibility between injected and formation waters and changes in temperature, pressure, gas dissolution and pH.

In the other hand, this is a process of deposition of scales from aqueous solutions of minerals, referred to brines, when they become supersaturated as the result of changes in the state of their thermodynamic and chemical equilibria.

In water injection process, mineral scale deposition generally occurs when foreign fluids (usually brines) are contacted with another one. Fluids rich in divalent ions such as calcium, magnesium, barium and strontium often tend to be the worst offenders in this area, even though their high divalent ion concentration may make them desirable for inhibiting formation damage from a clay swelling or deflocculation viewpoint. Mineral scale deposition causes serious damages in utilization...
systems and reduces flow areas. Well production and injection rates and capacities drop with consequent economical loss. For example, BP loses around 4 million bbls per year in the North Sea \(^{(2)}\). It can also plug production lines and equipment and impair fluid flow. The consequence could be production-equipment failure, emergency shutdown, increased maintenance cost, and overall decrease in production efficiency. The failure of these equipments could result in safety hazards \(^{(3-5)}\).

Biocorrosion, or Microorganism Influenced Corrosion (MIC), is a serious degradation process being faced by energy production and industrial sectors, mainly in the tropical, or subtropical climate countries. The microorganisms are arranged in a biofilm formed by the extracellular polymeric material (EPM) produced by them \(^{(6)}\). The production of organic deposits on the surface of equipment at, for example, hydroelectric power stations is often known as "biofouling". It can be present in stationary and fast flowing, or turbulent water. Usually, these deposits lead to a significant reduction in the efficiency and useable lifetime of the equipment. Many studies have been carried out on the MIC, but only few have focused on the process as it occurs in the contaminated water, or in the river (non-saline) water \(^{(7,8)}\).

Frequently, immersed metals suffer biological degradation (biocorrosion) as well as physical and chemical processes that lead to corrosion. Physical and chemical degradation can cause intense changes in the behavior of the metal/solution interface. All these processes occur at the same time and, as result, a new metal/solution interface is generated, which can accelerate the MIC. The corrosion and weathering caused by the biofilms can lead to reduced efficacy of heat exchangers, unexpected corrosion of stainless steel and premature destruction of mineral materials \(^{(9)}\).

Although there have been several studies about MIC over the last few years, biocorrosion processes are still poorly understood. Economic losses due to equipment damage by the biocorrosion are combined with those resulting from biofouling, where 70.3% of energy production originates from hydroelectric power stations. These stations can be seriously affected by biofouling and biocorrosion, especially given Brazil’s suitable climatic conditions for biofilm development in natural waters \(^{(10)}\).

The high energy ionizing radiation from radioactive souces such as \(^{60}\)Co or an electron beam accelerator has the ability to inactivate microorganisms present in waste water with a very high degree of reliability and a clean and efficient manner \(^{(9)}\). The ionizing radiation inactivate microbial cells both directly and indirectly.

Hydrogen peroxide \(\text{H}_2\text{O}_2\) and hydrogen molecule molecule \(\text{H}_2\) are also important products of the primary interactions during water radiolysis.

\[
\text{H}_2\text{O} \rightarrow \text{e}^-_{\text{aq}}, \cdot\text{H}, \cdot\text{OH}, \text{HO}_2 \cdot, \text{H}_2\text{O}_2, \text{H}_2
\]

The strong activated radicals made the radiation processing as a very effective option, since it can simultaneously degrade toxic organic compounds, as well as biological contaminants that are present \(^{(11)}\).

The main objective of the present work is to study the effect of gamma radiation and biocides on SRB count in presence of scale inhibitors in a trial to minimize the applied chemicals concentrations through water flooding techniques to eliminate the hazards of the chemicals used.

**MATERIALS AND METHODS**

1-Water Samples for Compatibility test:

The water samples collected from petroleum treatment plant in middle delta of Egypt. Twenty-liter samples were collected from each of 1. The formation water (FM) from petroleum well head with water cut about 75%. 2. Produced water (PM) from the outlet of the petroleum treatment plant which assigned to be used as injection water.
2-Water Samples for SRB count:

Sample was collected from produced water the outlet of the petroleum treatment plant in sterile glass containers (10 ml) which contain preservatives and oxygen scavenger to keep SRB available till the sample reach the laboratory.

3- Jar Test for Determination of Maximum Scales at different mixing ratios:

The collected virgin water samples to be tested for scale incompatibility are initially pre-filtered to remove any suspended materials. The brines are mixed to predefined ratio (FW: PW=20:80, 40:60, 60:40 & 80:20) and incubated at the 70 °C test temperature, 14.697 psi for 48 hours. After incubation, the mixtures were left for 24h then filtered through 0.42-micron filter paper to catch any precipitate. The filter papers were dried at 120 °C for 2 hours and then the precipitates were weighted. The maximum scaling ratio was determined based on the weight of the precipitates. The mixing combination ratios at which the maximum scale mass was formed at ambient conditions was named the worst mixing ratio.

4- Routine culturing method for sulfate reducing bacteria (SRB):

Most probable number (MPN) technique was used for detection and enumeration of sulfate-reducing bacteria in collected water samples using Starkey’s Medium (Modified) Containing: Sodium lactate 3.5 g, Ammonium chloride 1.0 g, Dipotassium hydrogen orthophosphate 0.5 g, Magnesium sulfate 2.0 g, Sodium sulfate 0.5 g, Calcium chloride 0.1 g, Thioglycollic acid 0.1, Ammonium ferrous sulfate 0.001 g and Water 1 liter. For MPN estimates, a 1-ml sample of each batch test was added to 10 ml of Starkey’s Medium (Modified), 1 ml of the resulting bacterial suspension was sequentially diluted by 10X increments to a final 10^6 fold dilution. Each series was performed in triplicate. Anaerobic dilution tubes were scored for SRB by noting the presence of a black FeS precipitate after 21 days at 30°C. MPN were determined using most probable number scales.

5- Scale Inhibitor Evaluation:

The above jar test was applied using two scale inhibitors (I) Supplied by petrolite and (II) supplied by Egyptian Canadian Company at concentrations of 5, 10, 15, 20, and 25 ppm which were added separately to the replica of 500 ml flasks of containing the water of worst mixing ratio.

6- Biocides Evaluation:

Each biocide activity was evaluated at different concentrations 100,200,300,400,500, and 600 ppm. The concentrations of the biocides were made using the water of worst mixing ratio containing optimum concentration of scale inhibitor in ten-milliliter glass vials which were purged with nitrogen gas. The untreated vial of mixed water sample was taken as negative control. The prepared vials were incubated at 30°C for two hours as contact time. One ml of each vial was inoculated in the above Starkey’s medium to determine the available count of sulfate reducing bacteria by the above MPN technique.

The efficiency of biocide was calculated according to the formula

\[
\% \text{ Efficiency} = \frac{a - b}{a}
\]

Where: 
- a: is the Sulfate reducing bacterial count without biocide
- b: is the Sulfate reducing bacterial count with biocide.

7- Gamma irradiation of Sulfate Reducing Bacteria in chemically treated produced water:

Different doses of gamma irradiation were applied on SRB within the mixed water. This mixed water contained the optimum concentration of scale inhibitor and sub-lethal concentration of biocides. Only five milliliter of the mixed water transferred to sterile vials purged by nitrogen gas, then exposed
to different doses: 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.2 kGy. Gamma irradiation process was carried out in gamma chamber 4000 irradiation facility (manufactured at Bhabha Atomic Research Center India). conducted in $^{60}$Co Indian cell located at National Center of Radiation Research & Technology, Nasr city, Egypt (NCRRT). The dose rate was 0.12 kGy / min.

For each treatment as well as control 0 kGy, the bacterial counts were determined in vials Starkey’s medium after incubation at 30 °C for 21 days through the MPN technique.

8- Testing of the treated water samples for oil recovery capacity:

Silica grains with size distribution of 80 to 120 μm were activated at 180 °C hot oven and mixed with base oil at ratio of 1: 25 / base oil: silica grains. Twenty five grams of this oily silica was added to 100 ml of each. 1- Original produced water samples as control and 2- Irradiated treated produced water representing the injection water. These microcosm were incubated on the shaker at 150 rpm and room temperature at 25 °C for 2 hours. The tested water samples were filtrated by Beckkman’s 42 filter paper. The recoverd hydrocarbons determined gravimetrically via solvent extraction by analytical grade chloroform.

RESULTS AND DISCUSSION

1- Determination of Maximum Scales at different mixing ratios using Jar test:

Jar test was applied using the tested scale inhibitor at concentrations of 5, 10, 15, 20, and 25 ppm. The data obtained were illustrated in Table (1). The data show that the maximum amount of scales formed at mixing ratio of 80 : 20 / produced water : formation water, this mixing ration was considered as the worst case mixing ratio.

Table (1): Maximum scale formed from mixing of Formation and produced waters at different mixing ratios.

<table>
<thead>
<tr>
<th>Percentage of Produced water (%)</th>
<th>Maximum scale formed (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>84.3</td>
</tr>
<tr>
<td>40</td>
<td>113.6</td>
</tr>
<tr>
<td>60</td>
<td>186.4</td>
</tr>
<tr>
<td>80</td>
<td>212.6</td>
</tr>
</tbody>
</table>

2- The Bacterial count of sulfate reducing bacteria (SRB):

The sulfate reducing bacterial count in water samples collected from petroleum treatment plant are represented in Table (2). The data showed significant count of SRB in the produced water sample, whereas, less amount of SRB in formation water. These results may be revealed that there were appropriate conditions for SRB growth among the petroleum treatment plant which support SRB flourishing.

Sulfate-reducing bacteria (SRB) are among the most destructive environmental organisms, and their industrial impact is widespread. They are present and cause corrosion and stress corrosion cracking of metals and alloys used in petroleum production and refining, cooling water systems, waste treatment systems, pulp and paper production,” and, in short, all aqueous processes$^{[14,15]}$. 

185
Table (2): The Sulfur Reducing Bacterial (SRB) count in water samples collected from different points of petroleum treatment plant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfate reducing bacteria count (cell/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation Water</td>
<td>5.6 X 10^2</td>
</tr>
<tr>
<td>Produced Water</td>
<td>6.2 X 10^6</td>
</tr>
</tbody>
</table>

3- Evaluation of the scale inhibitors:

The mixing ratio 80% produced water and 20% formation water was considered the worst case which was having the maximum scale formation. This ratio used for the evaluation of scale inhibitors at different concentrations.

Table (3) shows the data obtained from the evaluation of the scale inhibitor (I) and scale inhibitor (II), the data revealed that the Scale inhibitor (I) reach the maximum activity at concentration of 20 ppm, where as the maximum activity of scale inhibitor (II) at 30 ppm. So the scale inhibitor (I) is superior through SRB biocides evaluation at optimum dose of 20 ppm.

Scale inhibitors used in the oil industry generally fall into three main types: Inorganic Phosphates, organophosphorous compounds, and organic Polymers. There are many proposed mechanisms by which scale inhibitors operate.

Generally they interfere with either nucleation and/or with crystal growth. At the nucleation stage, threshold scale inhibitors bind with scale-forming ions, but unlike chelants, the bound ions must be available to interact with their counter ions. This disrupts the ion cluster at the early equilibrium stages of crystal formation, disrupting them before they reach the critical size for nucleation. As a result, the ions dissociate, releasing the inhibitor to repeat the process. At the growth stage, growth inhibitors slow the growth of the scale by blocking the active edges of the crystal.

Table (3): Maximum scale formed from mixing of Formation and produced waters at worst mixing ratio. (without and with scale inhibitor at different concentrations).

<table>
<thead>
<tr>
<th>Scale inhibitor concentration (ppm)</th>
<th>Type of Scale Inhibitor</th>
<th>Scale inhibitor (I)</th>
<th>Scale inhibitor (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Maximum scale formed (mg/L)</td>
<td>Scale inhibitor efficiency (%)</td>
</tr>
<tr>
<td>0 (Control)</td>
<td></td>
<td>212.6</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>178.3</td>
<td>16.1</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>145.2</td>
<td>31.7</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>126.7</td>
<td>40.4</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>125.4</td>
<td>41.4</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>119.3</td>
<td>41.1</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>118.6</td>
<td>41.4</td>
</tr>
</tbody>
</table>

II-Biocides Evaluation:
The data obtained by the evaluation of biocides as a treatment technique of SRB were represented in Figure (1) the data showed that the biocide 1A was more efficient than 1B with lethal doses 400 and 500 ppm respectively. These biocides were used at their sub-lethal doses for the study of the combined treatment with gamma radiation to maximize the efficiency of sulfate reducing bacteria treatment using the minimum effective dose of both radiation and biocides to eliminate the negative impacts of both the chemical biocides and gamma radiation.

The effect of glutaraldehyde, a commercial biocide widely used in paper and pulp industry Glutaraldehyde (1,5-pentanediol) is a non-oxidizing biocide which achieves its biocidal activity by involving the crosslinking of the outer proteinaceous layers of the cell in such a way that cellular permeability is altered. The bacterial cell is unable to undertake most, if not all, of its essential functions. The ability of the outer covering of the cell to transport nutrients to the cell and to remove waste products from the cell is hindered and cell death results\(^{(17,18)}\). Glutaraldehyde is widely used as an antimicrobial agent in a variety of applications such as in cooling water systems, paper-pulp industry, oil field operation, leather tanning industry, poultry industry, cosmetic field, microbiological field, food industry and medical area. The extensive use of this biocide is due to being non-corrosive to stainless steel, soft metals, rubber and glass\(^{(19)}\).

III- Gamma irradiation of chemically treated produced water:

Different doses of gamma irradiation were applied on SRB within the mixed water, this mixed water contained the optimum concentration 20 ppm of scale inhibitor (I) and sub-lethal concentration of biocides 300 ppm of biocide A or 400 ppm of biocide B. The data of SRB count were demonstrated in Figure (2). The data revealed that SRB counts were obviously decreased with increase of the irradiation doses in both produced waters containing Biocide A and Biocide B and had a lethal irradiation doses at 1 kGy for both biocides.

This combined treatment could minimize the doses of biocides sufficient to kill SRB water systems otherwise eliminate the hazards of commercial biocides used in petroleum and water systems. Both gamma radiation and electron beam can be used for disinfection purpose. The lethal dose vary between the two types of radiation, lower dose of gamma radiation is required relative to the electron beam to achieve the same pathogen removal \(^{(20)}\). The lethal dose also vary according to the pathogens
initial count, type of pathogens, previous treatment and sludge moisture content. The source of ionizing radiation that could be used for disinfection purpose are gamma radiation (cobalt-60 or Cesium-137) and electron beam (ebeam accelerators). In the opinion of radiation scientists, 3-5 kGy of ionizing radiation is adequate to completely inactivate pathogens in sewage sludge (21).

Radiation effects on living organisms are mainly associated with the chemical changes but are also dependent on physical and physiological factors. Dose rate, dose distribution, radiation quality are the physical parameters. The most important physiological and environmental parameters are temperature, moisture content and oxygen concentration. The action of radiation on living organisms can be divided into direct and indirect effects.

Normally, the indirect effects occur as an important part of the total action of radiation on it. on water molecules yielding radicals OH, e-aq and H. The action of the hydroxyl radical (OH-) must be responsible for an important part of the indirect effects (22).

Greez et al (23) reported that radiation was directly damaging the cellular membranes and adversely effect on enzymes, energy metabolism and many molecules of particular importance in biological function of the cell. It is now universally accept that the deoxyribonucleic acid (DNA) represents the most critical “target” for ionizing radiation. It indirectly affect “DNA” by interaction of radiation with water in the cell or surrounding the cell leading to formation of free radicals (hydrogen atoms H*, hydroxy radicals OH*, HO2* and hydrated electron e-aq. Which can diffuse for enough to reach and damage DNA (11).

**Fig. (2):** Effect of different gamma-irradiation doses on sulfate reducing bacteria count in presence of 20 ppm scale inhibitor I and 300 ppm biocide (A) or 400 ppm biocide (B).

**IV- Oil recovery capacity of the irradiated chemically treated produced water:**

Original produced water samples, chemically treated produced water and irradiated chemically treated produced water were evaluated as injection water for oil recovery. The data obtained gravimetrically via solvent extraction by analytical grade chloroform were illustrated in Figure (3).
The data showed that in general oil recovery capacities increase with increase of chemicals injected to produced water that may be attributed to the surface activity of the injected chemicals.

It is obvious that the radiation doses applied increase the oil recovery capacities that may be attributed to the oxidation of traces hydrocarbons found in produced water or oxidation of chemicals used in the water treatment such as scale inhibitors or biocides, the oxidation products could have some surface activity e.g. fatty acids.

It is reported that Chain oxidation constitutes one of the most efficient processes realized in radiation processing of wastewater. As a rule, saturation of wastewater with air is needed for chain oxidation. Radiolytic oxidation at a moderate dose leads to the formation of carbonyl, carboxyl, hydroxyl and/or peroxide groups in organic molecules. The conditions of irradiation can be specifically chosen to achieve chain oxidation of various pollutants\(^{(24)}\).

![Fig. (3): Oil recovery capacity of original produced water and produced treated waters by different techniques.](image)

**CONCLUSION**

The chemical biocides effective concentrations can be minimized in combination with irradiation doses. Increase of the oil recovery capacity of injected (produced) water by the irradiation and chemical treatment. This technology could be used for the water that are injected into reservoirs, and suitable for oilfield and pipeline operators, and presented a viable bacteria control method.
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