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**REVIEW OF PRODUCED WATER CHARACTERIZATION, AND ITS NORM CONCENTRATION**

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***Abstract:*** Produced water that has been reported to contain Hydrocarbons, inorganic ions, dissolved gas, metals, and chemical treatment, in addition to NORM activity concentration, is considered a harmful waste resulting from the petroleum extraction process according to the significant concentration of naturally occurring radioactive material (NORM) is frequently disposed into nearby areas, leading to the contamination that increases the possibility of human exposure to NORM in various pathways. This work aims to provide an inclusive review of the produced water characterizations and the NORM concentration activity and their behaviors in previous studies from oilfield companies around the globe. The results indicate that Ra isotopes, as the most radionuclides present in produced water, U-238, and Th232, were remarkably present in low amounts. However, oil extraction is increasing, which leads to more produced water being disposed of, which is a genuine concern for human health, so an in-depth study is recommended focusing on produced water treatment or re-use as management methods instead of being disposed into the environment. Furthermore, the NORM waste and its influence could be abridged by obeying the endorsed standard of IAEA and other environmental protection agencies.

***Keywords*:** Produced water, oil production, NORM, metals, environment.

1. **Introduction**

The major challenge in the recent oil industry is the unwanted production of water and gas; every day, approximately 300 million barrels of water are brought up to the surface together with oil and gas [1]. produced water represents an enormous waste stream because of several oilfield company operations. During the oil extraction process, a huge amount of water comes out of the wells to the surface with the crude oil, including both formation water and injected water into the wells to enhance the oil and gas recovery [2]. The first source of produced water follows the oil and gas extraction process, while formation water that exists below the oil layer then enters through the porous reservoir and comes out of the well mixing with the crude oil. This process leads to a reduction in reservoir pressure and resolves this problem by injecting water again into the reservoir system to maintain the hydraulic pressure [3]. This injected water presents the second source of produced water based on the fact that the more oil extraction there is, the more produced water. Furthermore, the origin of that unwanted water involves saline water that exists and resides in the layer below oil and gas due to its high density compared to those hydrocarbons. Generally, there are two sources of saline water: flow from the same hydrocarbon zone due to hydrocarbon production and flow from other hydrocarbon zones due to hydrocarbon migration [2]. This Saline water is called formation water and becomes produced water when it is brought up in addition to oil to the surface as a mixture. In some other cases and due to the reduction of pressure in the reservoir, this water will be injected again to maintain the hydraulic pressure and enhance the oil recovery. The injected water is usually from injector wells towards the formation, which directs oil to another well-called producer well, while the formation water or the injected water arrives in the producer wells. These wells start extracting hydrocarbons as well as producing water. This mixture contains, in addition to the water and oil, metals that have been reported in various studies, including Cr, Ba, Ni, Zn, Mg, Fe, Ni, Pb, and K [4],. Heavy metals are transformed from a dissolved state to particles in water under oxygenated conditions [5], along with radium and radon, treating chemicals, salt, and dissolved oxygen. The stream of produced water is considered the main waste in terms of size after the oil and gas facilities.[6]-[7]-[8]-[9]-[10]-[11]-[12].

Naturally, radiation exposure is present due to cosmic rays or naturally occurring radioactive materials (NORMs) that originate in the Earth's crust and are present everywhere in the environment [13]. Produced water has been reported to contain significant values of NORM.[14]-[15]-[16]-[17]. Almost all elements are constituents from stable nuclides; however, U and Th are unstable by nature [18], and will fade in time by disintegrations into other radioactive elements by emitting alpha and beta particles accompanied by gamma rays. A uranium-235 nucleus undergoes a series of 11 transformations to become stable lead-207. A thorium-232 nucleus goes through 10 transformations counting $Ra^{228}$ and $Ra^{224}$ to become stable lead-208.

A uranium-238 nucleus undergoes 14 transformations, including $Ra^{226}$and $Rn^{222}$, to become stable lead-206, in addition to $K^{40}$, one of the three isotopes of K, which is widely distributed identically with its isotopes, implying that the presence of K will be accompanied by $K^{40}$. $K^{40}$ disintegrates once into either $Ca^{40}$ or $Ar^{40}$ emitting β-particles (89%) or γ-photons (11%), respectively.

1. **Characterization of produced water in oil and gas fields:**
	1. **Oil:**

A previous study in the western united states reported an amount of 40mg/l to as high as 2000mg/l of oil and grease in produced water [19]. This organic material is present in produced water either in the form of dispersed oil, which consists of separated oil droplets suspended in water. The level of droplet oil is affected by different factors such as the oil density and the amount of precipitation [20]. Solubility decreases rapidly as the carbon number increases in a straight-chain saturated hydrocarbon molecule [21]. Table 1 describes the solubility of some of these hydrocarbon present in the oil, such as pentane, hexane, heptane, octane, and nonane. The oil is present in water and non-hydrocarbon material in a dissolved state.

The relation found between oil dispersed and dissolved oil is provided in the experiment done, while acidified oil dissolved samples were led to converting them into dispersed oil [21], the produced water contains more dispersed oil; however, the dissolved oil contains the high concentration toxic components [22]. Generally, the nonpolar organics in produced water are constantly toxic. The high compounds in dissolved oil that contribute to toxicity are aromatics and phenols [23].

* 1. **Inorganic ions:**

In conventional or unconventional wells, chloride and sodium were the most abundant in produced water; however, sulfate was the lowest inorganic ions [24]. Some produced water proprieties were identified according to inorganic anions and cations, such as conductivity is determined by all cations and anions, and Cl-and Na+ determines the salinity of a formation. A similarity in cations concentration was noticed in both conventional and unconventional wells. At the same time, sodium was considered the most cation present in produced water, with a percentage of 81% in water produced from conventional wells and 90% in unconventional wells; however, the concentration of the anion was different in both wells types. The chloride represents 97% of the anions present in water from conventional wells, while 66% was the amount of chloride present in unconventional wells and 32% bicarbonate [25]. Furthermore, the salinity of produced water is greater than that of seawater, therefore, denser than seawater [26].

**Table 1**

Solubility of hydrocarbons components in produced water [21].

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Compound | n-pentane | n-hexane | n-heptane | n-octane | decane |
| Solubility (mg/L) | 39 | 11 | 2 | 1 | 0 |

* 1. **Metals:**

Produced water may contain metal as Cr, Ba, Ni, and Zn, in addition to heavy metals, which were transformed from a dissolved state to particles in water under oxygenated conditions [27]. Metals concentration is proportional to the geological age and features [28]; the metals type and chemical content are also affected by factors like injected water volume and chemical composition [29]. The concentration of barium, sodium, iron, magnesium, potassium, and strontium in natural gas field production was reported at higher concentrations [30]. Some metals concentration values in produced water from an oilfield were founded to be as much as 50000 times seawater [27]. The formation of particulate from produced water was according to substantial quantities of metals such as Al, Fe, and Mn that will precipitate on contact with seawater, absorb heavy metals and other chemicals, and settle to the bottom, thus altering the transport of the contaminants in the produced water plume and potentially focusing their accumulation onto the sediments. An experiment done to understand the toxicity of heavy metals in produced water after discharging into seawater found that the infiltrated water samples had h high concentration while the concentration was low in the filtrated samples.

* 1. **Total dissolved solids TDS**

A significant level of TDS was founded in produced water [31]-[19]. Produced water from some field locations can have TDS values as high as about 400,000 mg/L [32]. As a comparison, typical seawater has TDS at about 35,000 mg/L [33]. Many factors can cause a variety of TDS concentrations, such as the difference between the geological basins and the produced water sources. In addition, the TDS concentration was founded to have a high value in conventional wells, more than the concentration reported from unconventional wells [25]. Table 2 provides the Concentrations of metals, hardness, salinity, TDS, and density of produced water from oilfield activities.

**Table 2**

Concentrations of metals, hardness, salinity, TDS, and density of produced water [34]-[35].

|  |  |
| --- | --- |
| Parameters | Range mg\L |
| NaClCoPbCuFeMnNiZnKMgAlSrTDSThe hardness of water,$ CaCO\_{3}$Density. $20^{˚}$ | 8800-18900016000-195000.003-0.0040.003-0.0030.001-16.94310-47700.058-17.20.015-0.0170.027-10.13100-95301530-3790˂PQL-12.5709-2450237.6804890-447781010-1070 |

* 1. **Total dissolved solids TDS**

Carbonates, clays, corrosion products, proppants, and sands are found as suspended solids from wellbore and production formation, the values of TSS present in produced water may change from area to area depending on the wellbore and formation condition. The TSS concentration has been reported in the range of 14-800 $mg.L^{-1}$ [36].

* 1. **Chemical treatment:**

In addition to its natural components, produced water contains chemical treatment; basically, it is chemical additives to the wells while drilling operation to treat or prevent possible operation problems while wells oil drilling and enhance the separation of oil and water after extracting oil mixed with produced water [37]. Including scale inhibitors, corrosion inhibitors, oxygen scavengers, biocides to mitigate bacterial fouling, asphaltene dispersants, paraffin inhibitors, defoamers, emulsion breakers, clarifiers, coagulants, flocculants [38]. The type of chemical additives is chosen depending on the well and the fuel characteristics by the manufacturers [39].

* 1. **Dissolved gas:**

The reservoir contains oil and water, in addition to gas that will come out of the wells with oil and water, the most common gas found in produced water are Oxygen, Hydrogen sulfide, and carbon dioxide [40], and the salinity and temperature of produced water decrease the solubility of these gases while it increases with pressure.

1. **NORM concentration in produced water**

The radioactivity concentration in a given volume of water represents the levels of radioactivity in produced water; the distribution of the reported levels in different areas are varied from one region to another due to the geological characteristics in each region. Table 3 resumes the values of radionuclides associated with produced water that has been reported in several regions in the world.

According to the results shown in table 3, we notice that Ra isotopes are the dominant radionuclides in produced water, especially $Ra^{226}$, $Ra^{228}$and $Ra^{224}$. $Ra^{226}$, which results in from$U^{238}$, decays into $Rn^{222}$ by emitting alpha and beta particles and gamma radiation to reach a stable state over 1600 years of half-life. $On the other hand, Ra^{228}$, and $Ra^{224}$ are daughters products of the $Th^{232}$ decays chain, which decays into$ Ac^{228}$, $Rn^{220}$ respectively; $Ra^{228}$ reaches the ground state by emitting beta particles and gamma rays with an estimated half-life of 5.75 years, while $Ra^{224}$ ends up in the stable state through decays by emitting alpha particles and gamma rays over 3.7 days of half-life. The $Ra^{224}$ is noticed as the lowest radium isotopes present in produced water because $Ra^{224}$ appears in produced water without its immediate parents $Th^{228}$, so that will die out within two weeks of secular equilibrium, the same period for $Ra^{226}$ to reach its secular equilibrium with $Rn^{222}$, $Po^{218}$, $Po^{214}$, $Bi^{214}$, and $Pb^{210}$, while $Ra^{228}$ considered as the quick radium isotopes that reach its equilibrium with $Ac^{228}$ withing two days.

**Table 3**

Activity concentrations ($Bq.L^{-1}$) of$ U^{238}$,$ Ra^{226}$,$ Th^{232}$,$ K^{40}$, and $Ra^{228}, Ra^{224}$ in produced water in different oilfields worldwide

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Radionuclides | $$U^{238}$$ | $$Th^{232}$$ | $$K^{40}$$ | $$Ra^{226}$$ | $$Ra^{228}$$ | $$Ra^{224}$$ | Ref |
|  |  |  |  |  |  |  |  |
| Congo$(Bq.dm^{-3})$ | <4.5×$10^{-3}c$ | <4.5×$10^{-3}c$ | - | 5.1c | - | - | [9] |
| Egypt | - | 39.9c | 66c | 19c | - | - | [41] |
| Iraq | - | 9.4c | 66.4c | 20.3c | - | - | [42] |
| Romania | (0.043-1.1) | (0.21-8) | (221-899) | (23-45) | - | - | [43] |
| Syria | - | 19.2c | 1460c | 186.2c | - | - | [44] |
| Ghana | (0.11-1.03) | (0.21-0.56) | (1.65-11.99) - | - | - | [45] |
| Ghana | - | - | (5.90-23.90) | (6.20-22.30) | (6.40-35.50) (0.78-7) | [46] |
| Nigeria | - | - | 39.8c | 8.9c | 8.1c | - | [47] |
| Nigeria | - | - | (9.08-155.22) | (2.01-13.19) | (0.75-12.30) - | [48] |
| US $(pCi.L^{-1})$ | - | - | - | (56-1494) | (69-600) | - | [49] |
| US | - | - | - | (30-2690) | (35-763) | - | [50] |
| US | - | - | - | (<0.002-58) | (0.02-59) | - | [51] |
| Azerbaijan | - | (ND-13.71) | (26.1-194.5) | (ND-101.7) | - | - | [52] |
| Poland | <30 | - | 75c | <2 | <2 | - | [53] |
| Texas | - | - | - | (0.1 − 5,150) | ND | - | [54] |
| Brazil | - | - | - | (0.012-6) | <0.05-12 | - | [55] |
| Norway | - | - | - | 3.3c | 2.8c | - | [56] |
| Norway | - | - | - | (0.5-16) | (0.5-21) | - | [57] |
| Syria  | - | - | - | 51.9c | 37.5c | (0.2-3.7) | [58] |
| Oman | - | - | (1522-1535) | (514-529) | - | - | [59] |
| Turkey | - | - | - | 6c | 3.17c | 2.83c | [60] |

**(): the range of the concentration, c: the average concentration, ND: below the detectible limits**

$Ra^{226}$ was noticed as the most Ra isotopes present in produced water in different studies from different areas [9],[41]-[42]-[43]–[44],[54]; one of the reasons can be due to its high solubility in water and its behavior preferring the aqueous state. Furthermore, $Ra^{226}$ is chemically similar to Barium Ba, Strontium Sr, Calcium Ca, and Magnesium Mg so that it becomes incorporated in group II sulfate or carbonate deposits and scale [18]; high precipitation of $Ra^{226}$ is reported with strontium and barium, which are taken part in the metals present in produced water, this result is according to various previous experiments that aim to find the correlation between radium isotopes and metals.[27]- [61]– [62], Radium was remarkable to be mainly coprecipitated with barium sulfate (RaBaSO) and strontium sulfate (RaSrSO4) [63]. Figure 1and 2 illustrate the $Ra^{226}$ and $Ra^{228}$ distribution in produced water, respectively; results observed according to radium isotopes distribution confirmed the abundance of $Ra^{226}$ in produced water compared with $Ra^{228}$.

$U^{238}$ and $Th^{232}$ concentrations are noticed from table 1 that were measured according to their progenies $Ra^{226}$and $Ra^{228}$ respectively [51],[60],[27],The absent of $U^{238}$,$Th^{232}$ in produced water in some studies ,[12],[46]-[48]-[49]–[50]-[51]. according to their chemical characteristics, they prefer the solid rock phase and do not dissolve in the aqueous or oily phase; as a result, both series remain with reservoir rock and may appear as a natural concentration just during drilling activities [18].

Results display a high value of $K^{40}$ activity concentration, of range (1.65-1460) $Bq.L^{-1}$ in produced water, owning to the fact that K isotopes are widely distributed in nature (abundance in the Earth's crust 2.1%), including K40 (0.0117%). However, $K^{40}$ concentrations in produced water are lower than the values found in soil samples around the oilfield area [65].



*Fig. 1.* $Ra^{226 }$*distribution in produced water from oilfield companies worldwide*



*Fig. 2.* $Ra^{228 }$*distribution in produced water from oilfield companies worldwide*

1. **Conclusion**

Produced water was reported to contain Hydrocarbons, inorganic ions, dissolved gas, metals, and chemical treatment, in addition to NORM activity concentration. Even though the low NORM concentration present in produced water compared with its levels in scale and sludge amount, the accumulation of radioactivity concentration in the environment through the disposal of produced water represents a serious concern that leads finally to human exposure and environmental contamination, so an in-depth study is recommended focusing on produced water treatment or re-use as management methods instead of being disposed into the environment. Furthermore, the NORM waste and its influence could be abridged by obeying the endorsed standard set by IAEA and other environmental protection agencies.

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**ОБЗОР ХАРАКТЕРИСТИК ПЛАСТОВОЙ ВОДЫ И КОНЦЕНТРАЦИИ ПРИРОДНЫХ РАДИОАКТИВНЫХ МАТЕРИАЛОВ В НЕМ**

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***Резюме:*** Пластовая вода, которая, как сообщается, содержит углеводороды, неорганические ионы, растворенный газ, металлы и химическую обработку, помимо концентрации активности ЕРМ, считается опасными отходами, образующимися в процессе добычи нефти, в соответствии со значительной концентрацией естественного радиоактивного материала (ЕРМ) часто выбрасывается в близлежащие районы, что приводит к загрязнению, которое увеличивает вероятность воздействия ЕРМ на человека различными путями. Эта работа направлена на предоставление всестороннего обзора характеристик пластовой воды и концентрации ЕРМ, а также их поведения в предыдущих исследованиях нефтяных компаний по всему миру. Результаты показывают, что изотопы Ra, как и большинство радионуклидов, присутствующих в пластовой воде, U-238 и Th232, присутствовали в удивительно малых количествах. Тем не менее, добыча нефти увеличивается, что приводит к удалению большего количества попутной воды, что представляет собой реальную проблему для здоровья человека, поэтому рекомендуется провести углубленное исследование, сосредоточив внимание на очистке или повторном использовании попутной воды в качестве методов управления, а не утилизация в окружающую среду. Кроме того, отходы ЕРМ и их воздействие можно уменьшить, если следовать утвержденным стандартам МАГАТЭ и других природоохранных агентств.

***Ключевые слова:*** Пластовая вода, добыча нефти, ЕРМ, металлы, окружающая среда.

**İSTEHSALAT SUYUNUN XARAKTERİSTİKALARI VƏ TƏBİİ MƏNŞƏLİ RADİONUKLİDLƏRİN KONSENTRASİYASI HAQQINDA İCMAL**

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***Xülasə:*** Təbii mənşəli radionuklidlərin (TMR) aktivliyinə əlavə olaraq karbohidrogenlər, qeyri-üzvi ionlar, həll olunmuş qazlar, metallar və kimyəvi emaldan ibarət olduğu bildirilən lay suları təbii mənşəli radioaktiv materialların əhəmiyyətli konsentrasiyasına görə neft hasilatı prosesi zamanı yaranan təhlükəli tullantı hesab edilir. Təbii olaraq yaranan radioaktiv materialın (TMR) tez-tez yaxınlıqdakı ərazilərə atılması, insanın müxtəlif yollarla TMR-ə məruz qalma ehtimalını artıran çirklənmə ilə nəticələnir. Bu iş lay sularının xüsusiyyətləri və TMR konsentrasiya aktivliyi, eləcə də dünya üzrə neft şirkətlərinin əvvəlki tədqiqatlarında onların davranışı haqqında hərtərəfli icmalı təqdim etmək məqsədi daşıyır. Nəticələr göstərir ki, Ra izotopları, lay sularında mövcud olan əksər radionuklidlər kimi, U-238 və Th232, təəccüblü dərəcədə kiçik miqdarda mövcuddur. Bununla belə, neft hasilatı artır və nəticədə insan səhhətinin əsl problemi olan daha çox lay sularının çıxarılması ilə nəticələnir, ona görə də lay sularının idarəetmə metodları kimi təmizlənməsi və ya təkrar istifadəsinə yönəldilmiş dərin tədqiqatların aparılması tövsiyə olunur. Bundan əlavə, AEBA və digər ətraf mühit qurumlarının təsdiq edilmiş standartına əməl edilərsə, TMR tullantıları və onun təsiri azala bilər.

***Açar sözlər:*** lay suyu, neft hasilatı, TMR, metallar, ətraf mühit.