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DETERMINATION OF RADIOACTIVITY PRODUCED WATER SAMPLES

F.Y. Humbatov

Institute of Radiation Problems of ANAS
hfamil@mail.ru

Abstract: In current article were reported results of chemical and radiochemical measurements from formation waters separated from oil pumped from approximately 700 m below ground near Baku, Azerbaijan. The results also include data from a formation water storage pond ("radium lake") where the waters are temporarily stored after oil is separated and then eventually disposed of by pumping into the Caspian Sea. It was obtained that, there is a relatively strong inverse relationship to bicarbonate and sulfate, the bicarbonate dependency appears stronger. The radium-bicarbonate relationship, however, suggests that carbonate precipitation in formation waters is significant and may be an important control on the radium concentration.

Keywords: Oil industry; formation water; Radium isotopes; NORM; Azerbaijan

1. Introduction

Oil and gas production and associated processing operations often results in the accumulation of naturally-occurring radioactive material ("NORM" or "TENORM" if technologically enhanced) at elevated concentrations in by-product waste streams. The ultimate sources of most of the radioactivity are from daughter products of uranium (^{238}U, ^{235}U) and thorium-(^{232}Th) that are naturally present in subsurface formations from which oil and gas are produced. NORM, in the form of scale, has been known for many years to occur in some oil and gas pipelines. Deep formation waters, often with high total dissolved solids, tend to be enriched in natural radium isotopes. When these fluids are brought to the surface, CO_2 may escape, resulting in a pH rise with the solubility products of many sulfate and carbonate species being exceeded. The result is often precipitation of scale deposits rich in the divalent alkaline earths Ca^{2+}, Ba^{2+}, Sr^{2+}, and Ra^{2+} (Wilson and Scott, 1992; Mackay and Heriot-Watt, 2003; Efendiyev G.H. 1953.) [1-3]. Radium, and its decay products, can occasionally be concentrated enough to be of human health concern because of their gamma radiation (Bernhardt et al., 1996; Smith et al., 1996) [4-5]. It is estimated that between 300,000 and 1,000,000 metric tons of NORM scale are produced each year in the oil/gas industry (Tomson et al., 2003) [6]. The primary radionuclides of concern in NORM wastes are ^{226}Ra (^{238}U series), and ^{228}Ra (^{232}Th series) as well as their respective daughters.

The production waste streams most likely to be contaminated by elevated radium concentrations include produced water, scale, and sludge. Spills or intentional releases of these waste streams to the ground can result in NORM-contaminated soils that may need to be disposed. Since radium is fairly soluble in saline waters, it can follow the produced water stream and accumulate in formation water storage ponds rather than all being retained in scale deposits. Thus, dissolved radium in formation waters either remains in solution in the produced water, precipitates out in scales or sludges, or is removed from the produced water during storage (e.g., precipitation, adsorption onto sediment components). Conditions that effect radium solubility and precipitation include water chemistry (primarily salinity), temperature, and pressure (Jens and Sebastian, 2002) [7].

NORM contamination of scale and sludge can occur when dissolved radium coprecipitates with other alkaline earth elements such as barium, strontium, or calcium. In the case of scale, the radium coprecipitates primarily with barium, to form hard insoluble sulfate deposits (barite) (Doerner H.A. and Hoskins W.M., 1925) [8]. Such scale typically forms on the inside of piping, filters, injection wellhead equipment, and other water handling equipment, but also can form as a coating on produced sand grains. In the case of sludge, radium can be present in several forms. It can coprecipitate with silicates and carbonates that form in the sludge, or it can be present as particles of barium sulfate scale that become incorporated into the sludge. NORM-contaminated sludge can accumulate inside piping, separators, heaters and other types of treatment facilities, storage tanks, and any other equipment where produced water is handled.

Formation waters that are sent to disposal ponds may consist of accumulated heavy hydrocarbons, paraffin, inorganic solids, and heavy emulsions. We report here results of chemical and radiochemical measurements from formation waters separated from oil pumped from approximately 700 m below ground near Baku, Azerbaijan. Our results also include data from a formation water storage pond ("radium lake") where the waters are temporarily stored after oil is separated and then eventually disposed of by pumping into the Caspian Sea. We also analyzed the associated sediment for radiochemical components. Our study was intended to investigate how radium fractionates between the pond water and sediments.

2. Study site and experimental

We have chosen a study location that represents one of the original sites for oil production in Azerbaijan (operated by Surachany PGOM, Petroleum Gas Obtaining Management). This site is located in the southeast portion of the Absheron Peninsula, near the capital city of Baku (Fig. 1).

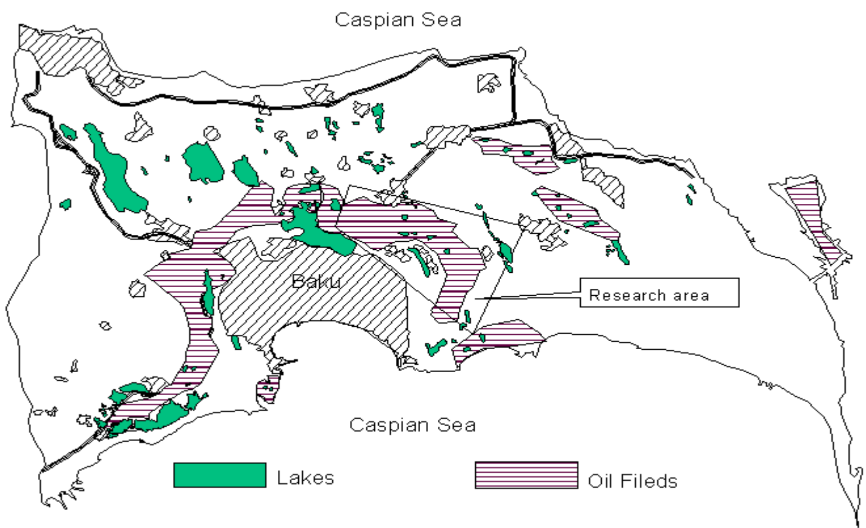

Fig.1. Map of Absheron peninsula showing site of oil field lake. (This site is located in the southeast portion of the Absheron Peninsula, near the capital city of Azerbaijan Republic -Baku. The petroleum began to be extracted at this site from the beginning of the last century -1907, with other sites in this area developing since 1912).

The petroleum began to be extracted at this site from the beginning of the last century (1907 with other sites in this area developing since 1912) (Alizadeh AA, Akhmedov GA, 1966)[9].

In recent years, the level of the deposits has been falling in the Surachany region requiring deeper drilling with lower grade deposits (higher percentage of formation water). At this site, as well as on other areas of the Absheron Peninsula some tens of hectares of polluted territories and lakes of petroleum origin are known to exist.

We collected samples of lake water, and formation waters from 7 different oil wells that surround the radium lake. All water samples were analyzed for major and minor cations (Na, K, Ca, Mg, Sr, and Ba) by atomic absorption spectrophotometry and anions (Cl, HCO_3, SO_4, Br, and I) by standard wet chemical techniques (B.Suleymanov et.al., 2008) [10]. We also measured the pH and total dissolved solids (TDS) for each water sample. Water samples were analyzed for ^{226}Ra, ^{228}Ra, and other radionuclides via gamma-spectrometry using a Canberra intrinsic germanium detector. All gamma spectrometric analyses were performed in silicone sealed Marinelli beakers after aging for one month to allow for ingrowth of ^{222}Rn and daughters. The photopeaks from the radon daughters ^{214}Pb and ^{214}Bi at 295, 352, and 609 keV were used to quantify ^{226}Ra and the ^{228}Ac peaks at 338 and 911 keV were used for ^{228}Ra (Burnett W.C. et.al.,2002; Landsberger S.et.al.,2013)[11,12]. Water samples were also analyzed for ^{222}Rn using a RAD-7 radon analyzer (Durridge Co., Inc.) with an attachment (RAD-H_2O) for analyzing radon-in-water. Uncertainties of the chemical measurements average about 5% and approximately 10% for the radioactivity measurements.

3. Results and discussion

General Situation

There are 86 wells operating in the immediate area around the formation water lake. These wells are pumping from an average depth of about 700 m and are recovering a very low grade oil deposit with most pumped fluids having an oil content considerably less than 2%. After separation of the oil the formation water is released to the "lake." These formation waters are all very high in total dissolved solids (> 70 to 160 g/L). While the in situ temperatures are approximately 60^o C, the water discharged to the lake is about 40^o C after separation. Approximately 3,000 m^3/day accumulates in this manner. When the level of the lake become too high, water is pumped into the Caspian Sea. Based on an estimated volume of the lake, the average residence time of the water is on the order of only a few months.

Well and Lake Waters

The formation waters in the lake and well samples are similar in almost all respects (**Tables 1 & 2**).

Table 1. *Concentration of cations and anions in well (W) and lake (L) waters. All samples filtered through a 0.45 μm filter except for the carbonate analyses.*

Sample N	Na mol/L	K mmol/L	Ca mmol/L	Mg mmol/L	Sr mmol/L	Ba mmol/L	Cond mS/cm	TDS g/l
1W	1.2	4.7	13	9	0.4	0.07	31.0	70
2W	1.2	6.4	7	11	0.6	0.03	33.9	73
3W	2.0	5.0	126	63	1.5	0.30	53.4	160
4W	2.0	4.1	120	47	1.3	1.30	50.1	140
5W	1.1	4.8	9	77	0.3	0.09	30.5	70
6W	2.1	5.2	130	66	1.5	0.20	53.9	160
7W	2.0	5.5	110	67	1.3	0.10	51.0	155
8L	1.3	4.4	25	26	0.5	0.08	34.6	80

Sample	Cl	SO4	HCO3	B	I	pH	Turb	Tot.Org
N	mol/L	mmol/L	mmol/L	μmol/L	μmol/L		NTU	g/L
1W	1.3	1.5	28	0.001	0.001	7.09	10	1.9
2W	1.3	1.2	70	0.001	0.002	6.89	40	17.5
3W	2.5	0.8	11	0.011	0.001	6.63	47	1.6
4W	2.3	0.7	7	0.001	0.004	6.22	35	3.0
5W	1.2	0.7	31	0.002	0.001	7.07	15	2.0
6W	2.6	1.2	12	0.001	0.001	6.34	23	0.9
7W	2.4	4.0	9	0.001	0.0004	6.09	54	2.2
8L	1.5	1.1	13	0.006	0.005	7.30	10.8	0.2

***Table 2**. Radionuclides in well (W) and lake (L) waters.*

Sample	Well depth	Ra-226	Rn-222	Ra-228	K-40
N	m	Bq/l	Bq/l	Bq/l	Bq/l
1W	646	1.4	16	2.5	3.8
2W	736	1.0	10.5	2.7	5.4
3W	649	2.0	45	4.5	4.3
4W	577	2.4	32	5.0	3.5
5W	737	1.4	5.3	2.0	4.9
6W	612	1.7	23	4.4	3.7
7W	707	2.1	16	4.2	5.7
8L	lake	2.3	6.4	3.8	11.5

They are all very high in TDS, mainly a sodium chloride brine with secondary calcium bicarbonate. All are in a pH range of 6-7. The waters are also very high in radium, with ^{226}Ra activities as high as 2.4 Bq/L and ^{228}Ra activities up to 5 Bq/L. Since "average" groundwater activities are typically around 0.015 Bq/L (Eisenbud and Gesell, 1997) [13], these waters are elevated by over two orders of magnitude. In general, the radium isotopes follow each other (Fig. 2) with an average activity ratio of 2.0±0.4.

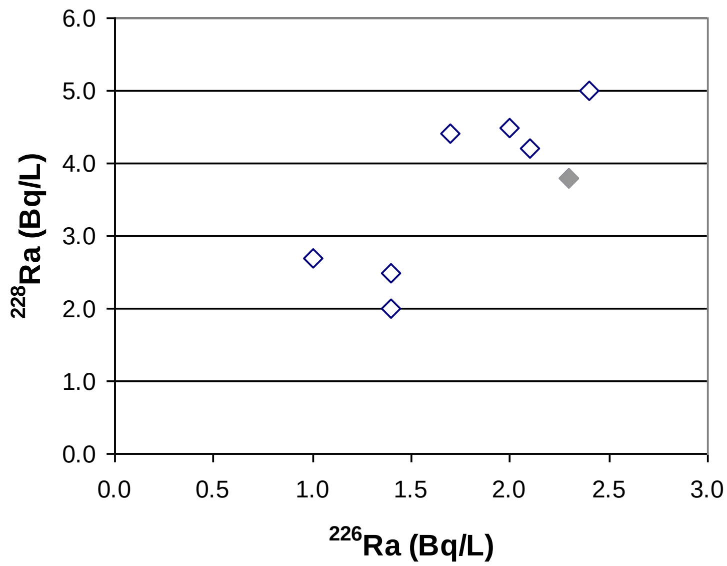

Fig. 2. Ra-228 versus ^{226}Ra in well waters and lake water. The open diamonds are well waters and the closed symbol represents the lake water.

Both ^{226}Ra and ^{228}Ra tend to be highest in the waters with the highest TDS (Fig. 3). The lake water displays an intermediate character in this respect as it does with many of the other characteristics. This may be a result of the relatively low residence time in the lake as this is just temporary storage until the water is pumped into the Caspian Sea.

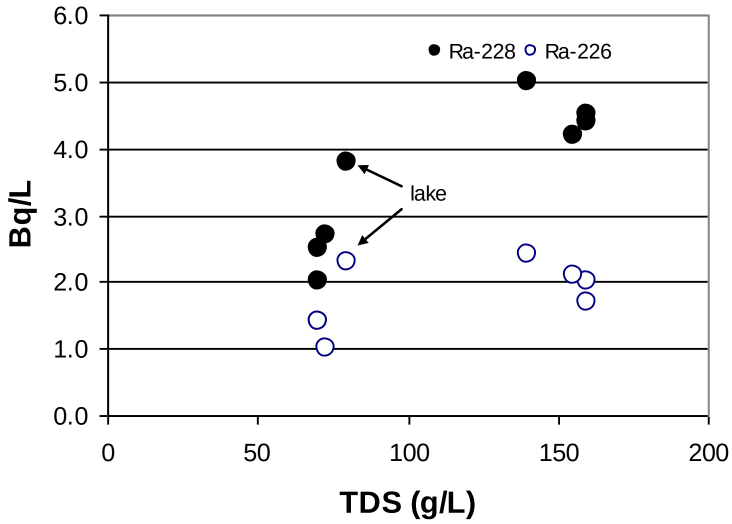

Fig. 3. Radium isotopes versus total dissolved solids.

While it is not clear what is controlling the radium content in these waters, we note that there is a relatively strong inverse relationship to bicarbonate (Fig. 4). While there is also an inverse relationship to sulfate, the bicarbonate dependency appears stronger. There is actually a somewhat positive relationship between radium and barium, which is surprising as barite ($BaSO_4$) is often thought to control radium solubility.

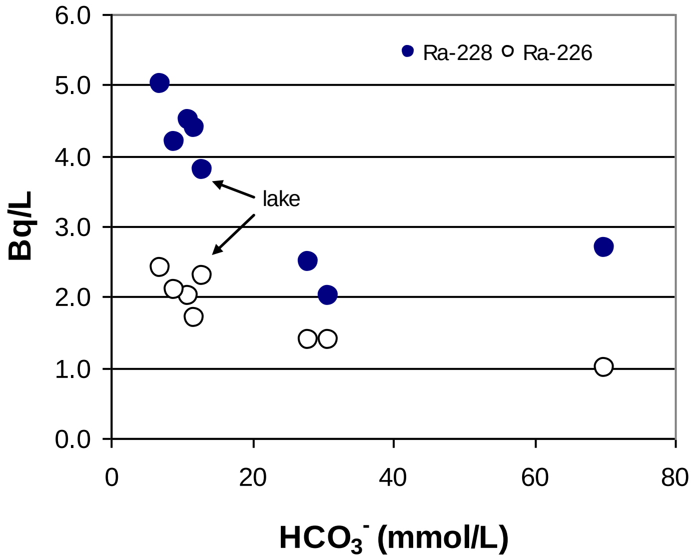

Fig. 4. Radium isotopes versus bicarbonate concentration. The outlier at 70 mmol/L HCO_3 may be a result of carbonate particles in suspension that consumed acid during the titration. Samples for carbonate analyses were run unfiltered.

It may be that there were fine particles of suspended barite in the water samples (samples for gamma spectrometry were filtered through a paper filter to remove oil residues, etc., but fine particles could have passed through). We entered the chemical data for the lake water (sample 8L) into the thermodynamic program MINEQL and it predicted that barium sulfate and calcium carbonate would precipitate. The program calculated that 99.6% of the Ba would precipitate out as $BaSO_4$, and 36.6% of the Ca as $CaCO_3$. Our chemical results show some Ba is in solution (0.4 μm filtered) so it seems unlikely that such a large fraction precipitated. The radium-bicarbonate relationship (Fig. 4), however, suggests that carbonate precipitation in these waters is significant and may be an important control on the radium concentration.

4. Summary

The investigated water samples are very high in radium, with 226Ra activities as high as 2.4 Bq/L and 228Ra activities up to 5 Bq/L. Both 226Ra and 228Ra tend to be highest in the waters with the highest TDS. There is actually a somewhat positive relationship between radium and barium, which is surprising as barite (BaSO4) is often thought to control radium solubility. There is a relatively strong inverse relationship to bicarbonate and sulfate, the bicarbonate dependency appears stronger. The radium-bicarbonate relationship, however, suggests that carbonate precipitation in formation waters is significant and may be an important control on the radium concentration.

Investigation of radium isotopes (226Ra and 228Ra), and useful parameters of formation water give important information about history and origin of NORM contamination. The radium-bicarbonate relationship may be an important control on the radium concentration, without expensive radionuclide analyses.

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LAY SULARI NÜMUNƏLƏRİNDƏ RADIİOAKTİVLİYİN TƏYİNİ

F.Y. Hümbətov

Xülasə: Hazırkı məqalədə, Azərbaycanda, Bakı yaxınlığında yerləşən və təxminən 700 m dərinlikdən çıxarılan neftdən ayrılan lay sularının kimyəvi və radiokimyəvi ölçmə nəticələri təqdim edilmişdir. Nəticələrə həmçinin, neftin ayrılmasından sonra lay sularının müvəqqəti saxlanıldığı və sonra Xəzər dənizinə nasosla axıdıldığı süni göl ("radium göl") məlumatları da daxildir. Radium konsentrasiyasının bikarbonat və sülfatlardan güclü tərs asılılığı mövcuddur, bikarbonat asılılığı daha güclü görünür. Radium-bikarbonat əlaqəsi, lay sularında karbonat çökməsinin əhəmiyyətli olduğunu və radium konsentrasiyası üzərində əhəmiyyətli bir nəzarət ola biləcəyini göstərir.

Açar sözlər: Neft sənayesi; lay suyu; Radium izotopları; TMRN; Azərbaycan

ОПРЕДЕЛЕНИЕ РАДИОАКТИВНОСТИ ПРОИЗВОДСТВЕННЫХ ВОДНЫХ ОБРАЗЦОВ

Ф.Ю. Гумбатов

Резюме: В настоящей статье были представлены результаты химических и радиохимических измерений пластовых вод, отделенных от нефти, перекачиваемой с примерно 700 м ниже грунта находящихся не далеко от Баку, в Азербайджане. Результаты также включают данные из водохранилища пластовой воды («озеро радия»), где воды временно хранятся после отделения нефти, а затем в конечном итоге удаляются путем закачки в Каспийское море. Было получено, что существует относительно сильное обратное отношение изотопов радия к бикарбонату и сульфату, зависимость бикарбоната проявляется сильнее. Однако отношение радий-бикарбонат указывает на то, что осаждение карбонатов в пластовых водах является значительным и может быть важным контролем концентрации радия.

Ключевые слова: Нефтяная промышленность; пластовая вода; Изотопы радия; ЕРН; Азербайджан