Radioactivity Reduction Technologies for Frac and Produced Water

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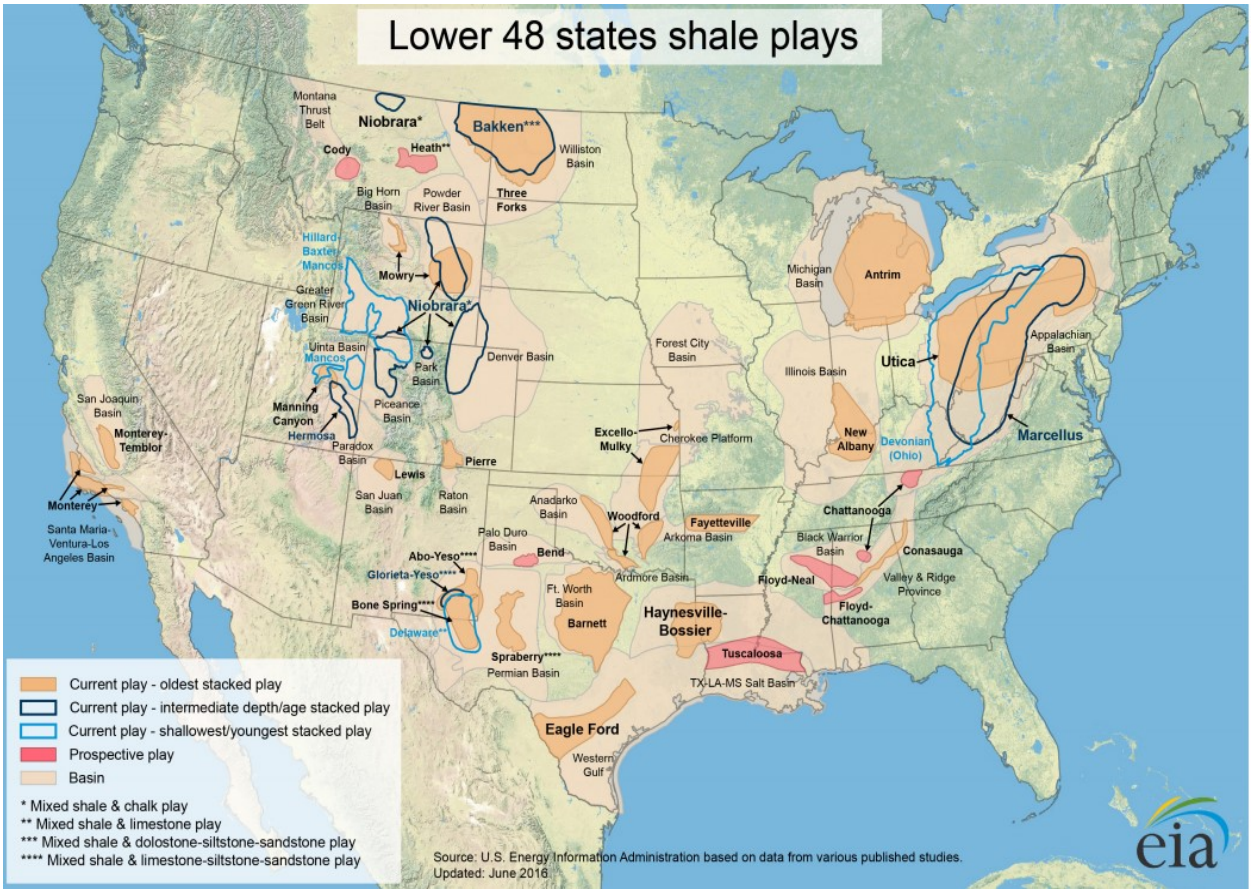
1. Introduction

In the oil and gas (O&G) industry, radioactive materials known as "Naturally Occurring Radioactive Materials" or NORM, can be brought to the surface through O&G wells. This happens when the formation fluids pumped out of the well that contain elevated concentrations of radioactive materials (radionuclides) such as uranium, thorium, radium, strontium 90, americium, etc. Not every O&G well is radioactive nor does every well produce radioactive frac and produced water streams. However, every O&G well results in flow back water that contains varying concentration of dissolved salts (TDS). Presently, there are around 1,057 active onshore and offshore O&G rigs in the US. The top ten O&G shales are listed in the following link and figure:

https://www.wpowerproducts.com/news/10-biggest-shale-plays-in-the-us-revised/.



The author designed numerous frac and produced water (FPW) treatment facilities in 8 out of the 10 biggest US shales. Based on his experience, over 2% of O&G wells produce elevated concentrations of radionuclides and the salinity levels vary from as low as 10,000 ppm in Bakken to as high as 240,000 ppm in Marcellus. The higher the salinity, the more NORM is likely to be mobilized. Since salinity often increases with the age of a well, old wells tend to exhibit higher NORM levels than younger ones.

The presence or absence of radionuclides themselves does not necessarily classify the O&G exploration wastes as USEPA hazardous or non-hazardous. The following link refers to the USEPA definition of wastes:

https://www.epa.gov/radiation/radiation-basics

Since untreated frac and produced water cannot be discharged directly into the public sewer collection systems or waters of the states, O&G exploration companies ship low-level radioactive waste (LLRW) or hazardous waste mixed with LLRW (a so-called "mixed waste"), sometimes across the country, to licensed facilities. Presently, LLRW is accepted by very few facilities in the US, one of which being Envirocare in Clive, UT. Despite frequently fluctuating costs of oil and gas, the findings of high-level radioactivity in the Marcellus (PA) and other shales trigger higher disposal costs and stiffer transportation regulations.

It should be emphasized that NORMs are not *normal* just because they are naturally occurring at 2,000 ft - 3,000 feet below the surface. On the surface, they are not part of the normal environment and should be treated as hazardous. Because the radioactive materials become concentrated on the field equipment, the highest risk of exposure to oil and gas NORM is for workers who cut and ream oilfield pipe, remove and dispose of solids from tanks and pits, refurbish crude oil and gas-processing equipment, drive trucks to dispose of the process water and solids, and all others all who are in contact with any equipment, product and material exposed to radioactive material. Presently, none of the O&G field operators tests their workers and especially their family members for radioactive exposure.

Radioactive materials emit alpha, beta, gamma and x-ray radiation depending on the atomic number (AN) of the emitting radionuclide and the origin of the radiation. The nuclides with the AN below 91 such as strontium (^{90}Sr) usually emit beta-radiation and above it – alpha, such as radium (^{226}Ra) and uranium (^{238}U). Gamma radiation is emitted from the nucleus when struck by a neutron and x-ray radiation originates from the outer electron shell. Alpha, beta and neutron are particles (i.e. they have mass) emitted from atoms whilst gamma and x-ray are photons of energy which don't have mass. These types of radiation are collectively called ionizing radiation versus non-ionizing radiation (microwave, laser, welding, etc.). Alpha radiation is an internal hazard (such as when ingested) but can be stopped by a single sheet of plain paper. The range of gamma and beta radiation is up to 1 km and 15 meters in air, respectively. The most common protection from beta is lucile or similar plastics, paraffin – for neutrons and for gamma – water, lead and concrete. The radiation dose and radioactivity are measured in mR or mSv per unit of time and pCi or Bq per unit volume or mass, respectively.

2. Regulatory FPW Discharge Limits for Radioactivity

If a treatment system has material that contains more than 0.05 percent uranium or thorium (but not radium) by weight and has a total of no more than 15 pounds in its possession at any time, it is considered to have a "small quantity" of source material (10 CFR 40.22) and is subject to the general license requirements of 10 CFR 40.22 or equivalent regulations of the Agreement States. Under this general license, systems may not possess more than 150 pounds of source material in any one calendar year. This material held under this general license normally also requires disposal at facilities authorized to accept LLRW. Systems that exceed these small quantity thresholds must apply for specific licenses from the NRC or Agreement State and dispose of residuals at facilities authorized to accept LLRW unless regulators approve another type of disposal. FPW water treatment facilities that exceed the small quantity thresholds can apply to the NRC for an exemption from regulatory requirements in 10 CFR Part 40.

Most of the states with O&G drilling activities don't have FPW surface water or aquifer discharge limitations for radioactivity other than the federal MCL (Maximum Contaminant Levels) for drinking water of 5 pCi/L for Total Radium and 30 µg/L for Total Uranium. For comparison, in Marcellus the FPW has been found to contain up to 16,000 pCi/L of Radium-226 alone. Any FPW stream that contains TDS in excess of 10,000 ppm and radioactivity above the MCL level has to be treated before it can be discharged into the surface waters or a publicly owned treatment works (POTW). The cost of treatment is prohibitive for many small- and medium size field operators. Because of that, the major portion of FPW in hauled to the states where one or more of the following options is applicable:

1. Dilution to 1%-2% (10,000 ppm – 20,000 ppm) of salinity and discharge to a POTW
2. Dilution to 1,000 ppm TDS and the pCi/L level defined by the state for surface water discharge
3. Underground injection of FPW
4. Indefinite storage of FPW in lined lagoons
5. Water recycling, if cost is lower than local
6. Water reuse for fracking, if cannot be used locally.

In many states (e.g. NY), Option (3) is not readily available. In Texas and Oklahoma, this is still an option. Transportation costs, however, usually reduce the number of options to zero often leaving the operator with the following choices:

a. Dilution (3:1), partial volumetric treatment and storage if reopen the well in the near future
b. Dilution (2:1), disinfection and reuse for drilling with loss of quality (shown in figure below)
c. Evaporation ponds when feasible, mostly in Gulf Coarse and California
d. Mechanical evaporation, e.g. MVR and Multi Flash Distillation
e. Membrane Distillation (MD) using high efficiency photovoltaic (PV) cells
f. Electrochemical methods such as capacitive deionization or electrodialysis reversal
g. Radionuclide adsorption, TDS remains
h. Cryogenic technology, e.g. freezing for TDS removal only
i. Reverse and Forward Osmosis (RO, FO).

Options (d) and (e) concentrate the radionuclides in salt (used as deicers) and centrate, respectively, but are expensive to install and run. Options (e), (f) and (i) are not economically feasible for large volumes of FPW and high TDS concentrations (i). Option (h) reduces salinity and the radionuclides concentration since a significant portion remains on salt crystals. Option (g) is capable to remove Ra and U from FPW and is economically feasible when the adsorbent is procured, supplied, regenerated and disposed of at a reasonable cost. Option (g) is discussed in more detail in the following sections.

In New York and Pennsylvania, the effluent discharge limit for Radium-226 is 60 pCi/L.

The Pennsylvania Department of Environmental Protection (PADEP) under their solid waste regulations define 2 action levels with respect to FPW radiation dose:

a. Action Level 1 when no action is required, and the waste can be treated as normal if the average background dose is below 10 mR/hr. A dose above average background of 10 mR/hr sets the gate alarm 'on' and the frac water haul trucks at the landfill are turned around.

b. Action Level 2 is triggered when the average background dose is above 2 mR/hr in the haul truck cab and 50 mR/hr on any other surface of the truck. The landfill must isolate the waste and/or the vehicle and promptly notify the PADEP.

According to PADEP, treated frac water sludges emit from 6 to 250 mR/h [1] and occasionally trigger Action Level 2.

The photos below show FPW haul trucks entering landfill radiation check points in Pennsylvania (PA).

GM and scintillation counters do not detect alpha-radiation at the distances shown on the photos above. Consequently, if the radioactivity in the waste sludge or spent material is due to alpha radiation alone as in the case of radium and uranium, the landfill operator must use a portable detector (such as those with a ZnS film).

According to the US Department of Transportation (USDOT) regulations, a cargo should carry less than 270 pCi U/g. The US EPA Underground Injection Rule (UIR) limits Radium 226/228 to less than 60 pCi Ra/L and Uranium to less than 300 pCi U/L for the purpose of disposal.

The US Nuclear Regulatory Commission (NRC) includes Radium (Ra) but excludes Uranium (UVI) and Thorium (Th) from the TENORM (Technologically Enhanced NORM) definition. However, the USNRC excludes Ra as a source but includes U and Th as sources for the purpose of LLRW definition. Two conditions need to be met in order to define U and Th as sources:

- Condition 1: U and Th make up > 0.05% of disposed mass, i.e. > 335 pCi/g of natural U/Th, and
- Condition 2: totaling more than 15 lbs of natural U/Th in bulk material.

The same conditions are applicable to other wastes such as, for example, potable water treatment sludge.

In 10 CFR Part 20, Appendix B, Table 2, the NRC defines radioactive waste as waste exceeding 60 pCi/L for both Radium 226 (most of Ra) and Ra 228, and 300 pCi/L for Uranium 234, Uranium 235 and Uranium 238 (most of U). These fractions can be expressed as follows:

$$f(Ra_{Total})/60+f(U_{Total})/300 = f(^{226}Ra)/60+f(^{228}Ra)/60+ f(^{234}U)/300+f(^{235}U)/300+ f(^{238}U)/300 \leq 1$$

As such, when the concentration of radioactive material exceeds 1, the final material is TENORM. It is also a LLRW if it meets the two conditions above for U and Th.

Depending on the point of discharge, the treated effluent quality may be required to be equal to that of drinking water. For instance, the International Commission on Radiological Protection (ICRP) guidance levels for radionuclides in drinking-water for Ra and U are 1 and 10 Bg/L, respectively. The ICRP IDC (Individual Dose Criterion) is equal to 0.1mSv/year. Screening levels for drinking water below which no further action is required are 0.5 Bq/L for gross alpha activity and 1 Bq/L for gross beta activity.

3. NORM in Marcellus and Barnett Shales

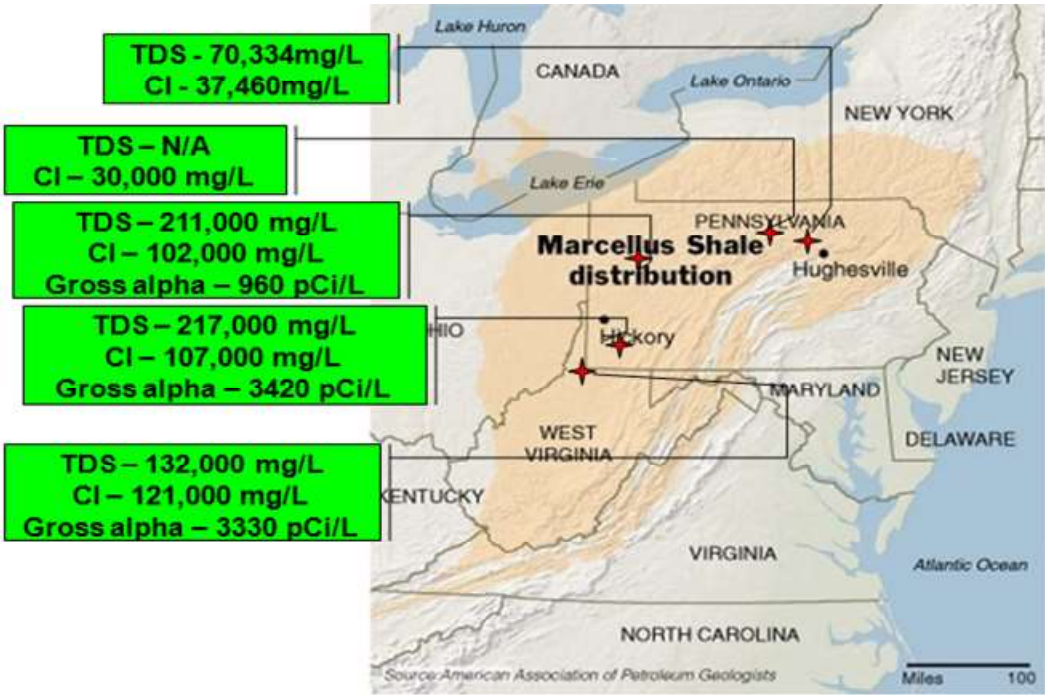
According to the Texas Department of State Health Services, 140 sites with high levels of NORM (either well sites or sites containing oil and gas equipment) were decontaminated between January 2005 and November 2007. Twenty five of the decontamination sites were in Denton, Tarrant and Wise counties, the core counties of the Barnett shale [4].

The Marcellus shale is considered to be the most “highly radioactive” shale in the USA (perhaps due to the amount of attention caused by ongoing public concern in regard to process water and solids disposal).

The New York Department of Environmental Conservation (NY DEC) analyzed 13 samples of returned drilling wastewater (flowback) from vertical Marcellus shale wells in Schuyler, Chemung, and Chenango Counties that contained levels of radium as high as 267 times the discharge limit and thousands of times the limit for drinking water [6]. The DEC also reports that the EPA measured values of radioactivity for flowback water of 9,000 picocuries per liter (pCi/l), or 9,000 times the natural radiation in normal well water and more than 100,000 picocuries per gram (pCi/g) for pipe and tank scale, or about 1,000 times the radiation level given off by normal concrete.

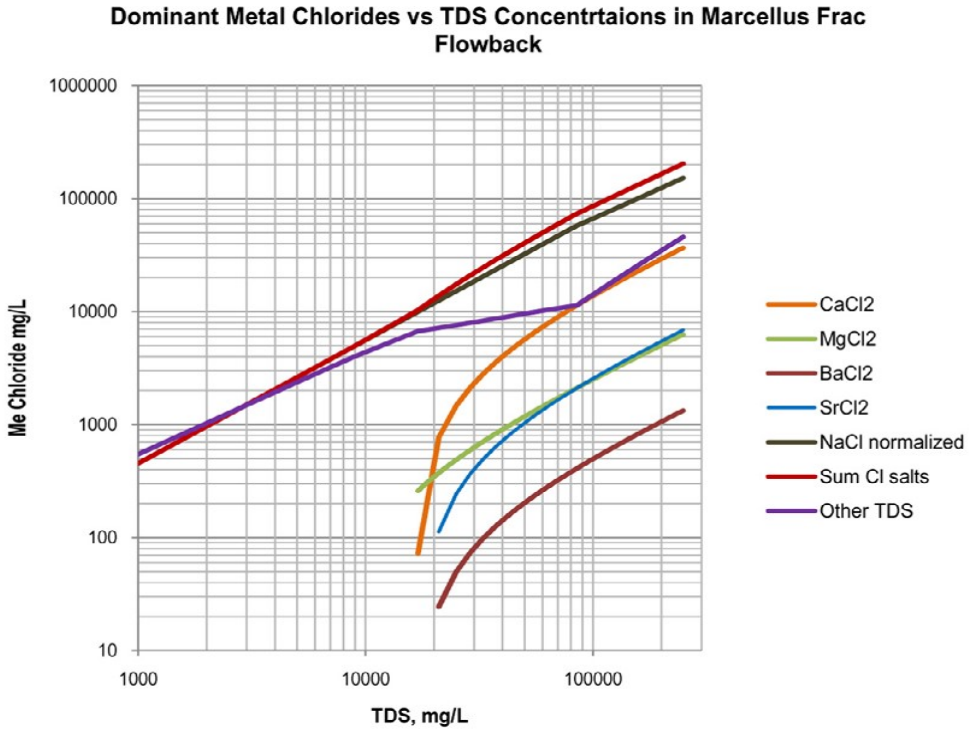
It should be noted again that currently there is no water quality regulation in PA or any other state of the US that would mandate certain alpha- and beta-radioactivity levels in frac flowback effluent. The effluent must meet certain water quality criteria (most often MCL) for radioactivity before it’s discharged in the environment or centralized municipal sewer systems. The author’s personal experience with Marcellus demonstrates that frac flowback and especially produced waters occasionally contain elevated levels of both alpha- and beta-radiation [2]. The figure below indicates some of the alpha-activity values.

Radionuclides such as radium, barium and strontium can be removed in the pretreatment step using the conventional water treatment technologies, e.g. cold lime softening (CLS), co-precipitation, and physical sorption onto aluminosilicates, zeolite, mica, ion exchange resin, or activated carbon. Uranium 238, which is the dominant alpha radionuclide in frac flowback, cannot be efficiently removed by CLS or co-precipitation. Several technologies for uranium 238 removal are listed below. They, however, have not been applied in the field of O&G exploration and frac flowback treatment due to large scale of operations.



1. SES (Capacitive Deionization/Selective Electrosorption using carbon nanofibers and aerogels)
2. Electrodeposition (reverse galvanic cell)
3. Precipitation (physical-chemical adsorption) using metal oxides/hydroxides/hydrites (e.g. TiO_2, $FeO{\cdot}Fe_2O_3$, α-FeOOH, y-MnO2). Uranium will precipitate as the sulfate and phosphate under acidic pH and as the carbonate under alkaline pH conditions, using NaOH, NH_4OH, $(Fe)_2(SO_4)_3$, $CaCO_3$, $(NH_4)_2SO_4$, $FePO_4$ H_3PO_4, H_2O_2, H_2SO_4, etc.
4. Adsorption on monosodium titanate (MST), silica gel, activated carbon, graphite, chitosan, zeolite, graphene, bentonite, kaolinite, montmorillonite, quartz, silt, mica, and mulch.
5. Ion Exchange (IX).

Elevated levels of alpha and beta radioactivity in salts resulting from MVR (mechanical vapor recompression) and other thermal treatment processes (such as multi-flash distillation, MFD) should strongly correlate to the levels of uranium, thorium, radium and strontium in produced water. Unfortunately, no data to define this correlation is publicly available. The figure below shows the average flowback chloride concentrations for 29 gas production wells in Western Pennsylvania [2].



The values shown in the table below are based on the data used in the URS Corporation Marcellus Report to the State of New York [5].

Radionuclide	No samples	Number of detects	Min Value (pCi/L)	Median Value (pCi/L)	Max Value (pCi/L)	US Drinking Water Standard - MCL (pCi/L)	Median Value/MCL Ratio
Alpha radiation (pCi/L) $^{4}{}_{2}\alpha$	25	6	22.41	**1,414.5**	18,950	15	94
Beta radiation (pCi/L) $^{0}{}_{\pm1}\beta$	25	6	9.7	**1,395**	7,445	50 (4 mR/y)	28
[^{226}Ra + ^{228}Ra] (pCi/L)	22	3	7.7	9.7	24	5	2
Uranium$_T$ (pCi/L)	NA	NA	NA	NA	NA	30 (20 ppb)	NA
Strontium 90 (mg/L)	30	27	0.5	821	5,841	10	82
TDS, mg/L	58	58	1,530	93,200	337,000	500	184
Ba (mg/L)	34	34	0.55	662	15,700	10	66
Chloride	58	58	287	56,900	228,000	250	228
Sulfate	58	45	0	3	1,270	250	0.01

Albeit the report does not provide any indication of the presence of thorium and there is no data on uranium, the amount of radium is clearly negligible. This implies that most of the alpha activity is due to Uranium (VI). According to the USGS, the gross alpha activity in Marcellus flowback water is 20,800 pCi/L, half of which is due to Radium 226 (10,200 pCi/L), only 48 pCi/L due to thorium, and the rest is contributed by Uranium 238. If we, therefore, suggest that 50 percent of alpha-radiation in the above table is due to Uranium 238 (^{238}U), then using the salt volumes from the previous table, the Avogadro number, the ^{238}U half-life, and the decay rate (from the definition of curie), the average per well mass of uranium in flow back frac water is as follows:

Median-value	Vertical Well	Horizontal Well
^{238}U, gram	136	406
Total α-emitters (Am^{241}, Pu^{244},Ra,Th^{232},U), gram	272	817

Rough 2013 landfill disposal costs for LLRW and TENORM waste resulting from treatment of Marcellus FPW vs regular solid waste is given in the following table.

Description	Vertical Well	Horizontal Well
Flowback, MGal (median value)	0.32	0.66
TDS, mg/L (median value)	93200	93200
Weight of salt, ton	124	255
Volume of salt, ft^3	3307	6800
Volume of salt, gal	24734	50864
Number of 110-gal drums	225	463
Container cost, $	56,214	115,750
LLRW disposal rate in Clive, UT, $/$ft^3$	155	155
Landfill disposal cost, $	513,000	1,045,000
Number of 20-ton trucks	6	13
Transportation cost (at $2.30/mi based on round trip), $	36,432	78,936
Total disposal cost (excluding documentation fees and taxes) as LLRW	$ 605,646	$ 1,239,686
Total disposal cost (excluding documentation fees and taxes) as TENORM (at $420/bbl [4])	$247,340	$508,380
Disposal cost as regular waste	$25,800	$53,850

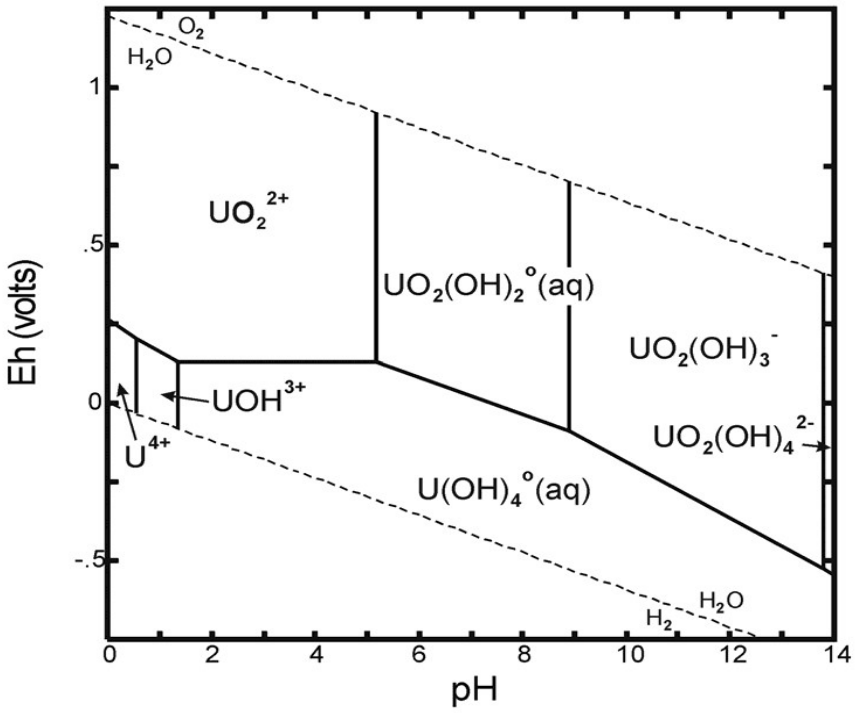
4. Uranium 238 Adsorption

The uranium (UVI) chemistry and its aquatic speciation is more complex than those for the rest of the alpha-emitters (radium and thorium) found in frac flowback and produced waters. Aqueous uranium speciation and its complexation is strongly dependent on the pH rather than its concentration. Unlike

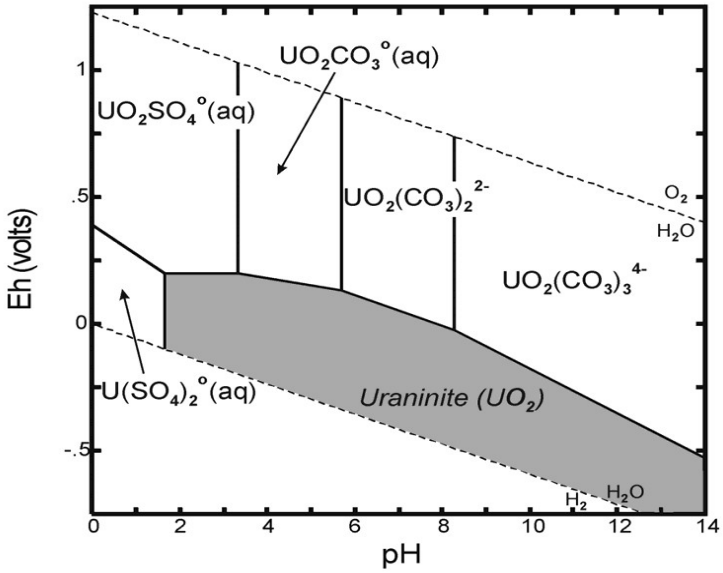
uranium, radium and thorium can be precipitated using the conventional means e.g. lime softening as a pretreatment step. One of the most significant drawbacks of pH adjustment is that, in addition to radium and thorium, the resulting sludge would contain numerous metals, such as barium, that will render this sludge not only radioactive but also toxic and hazardous making its handling and disposal even more costly.

Thorium precipitates at concentrations greater than 10^{-9} M and pH above 5.5 as $Th(OH)_4$. This concentration is based on the solubility of $Th(OH)_4$ at pH 5.5. Thorium adsorption occurs at concentrations less than 10^{-9} M. The extent of thorium adsorption can be estimated by the adsorbing media pH.

The following figures shows that uranium may be precipitated as $(NH_4)_2U_2O_7$, U_3O_8, UO_2, UO_3, $UO_2(OH)_2$, $NaO{\cdot}(UO_3)_2{\cdot}6H_2O$, $Na_2U_2O_7{\cdot}6H_2O$, $(UO_4{\cdot}nH_2O)$, UO_2SO_4, and $UO_2(CO_3)$.

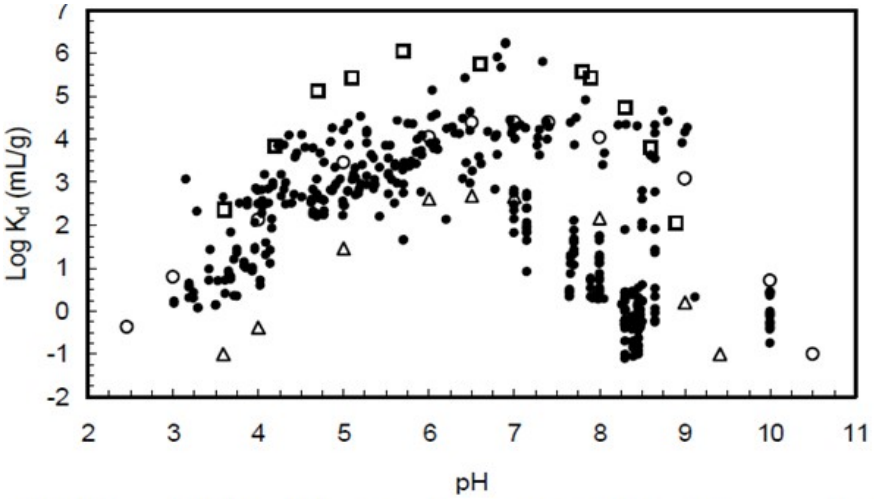


Above pH7, U is negatively charged and the carbonates dominate. Below pH7, U (VI) is charged positively and the sulfates dominate. U reduction to elemental metal is not possible because its reduction potential is more negative than that of water. Since the average Marcellus Shale frac flowback tends to be around neutral and there is little sulfate, the expected aqueous U (VI) species will be the chloride, hydroxides and some oxide if the carbonates are removed in pretreatment. For uranium chlorides, the previously described physical sorption processes alone are not very efficient. Selective electrosorption (SES/CDI) using carbon nanofibers would be the most efficient technology for U reduction. The following diagram demonstrates removal of uraninite as function of pH and voltage difference between the electrodes.



For ^{238}U, if the alpha radiation level in pCi/L in frac flowback 3 times exceeds the concentration of TDS in mg/L, then the solids resulting from evaporation/crystallization of frac flowback from one oil well is most likely a low level radioactive waste (LLRW).

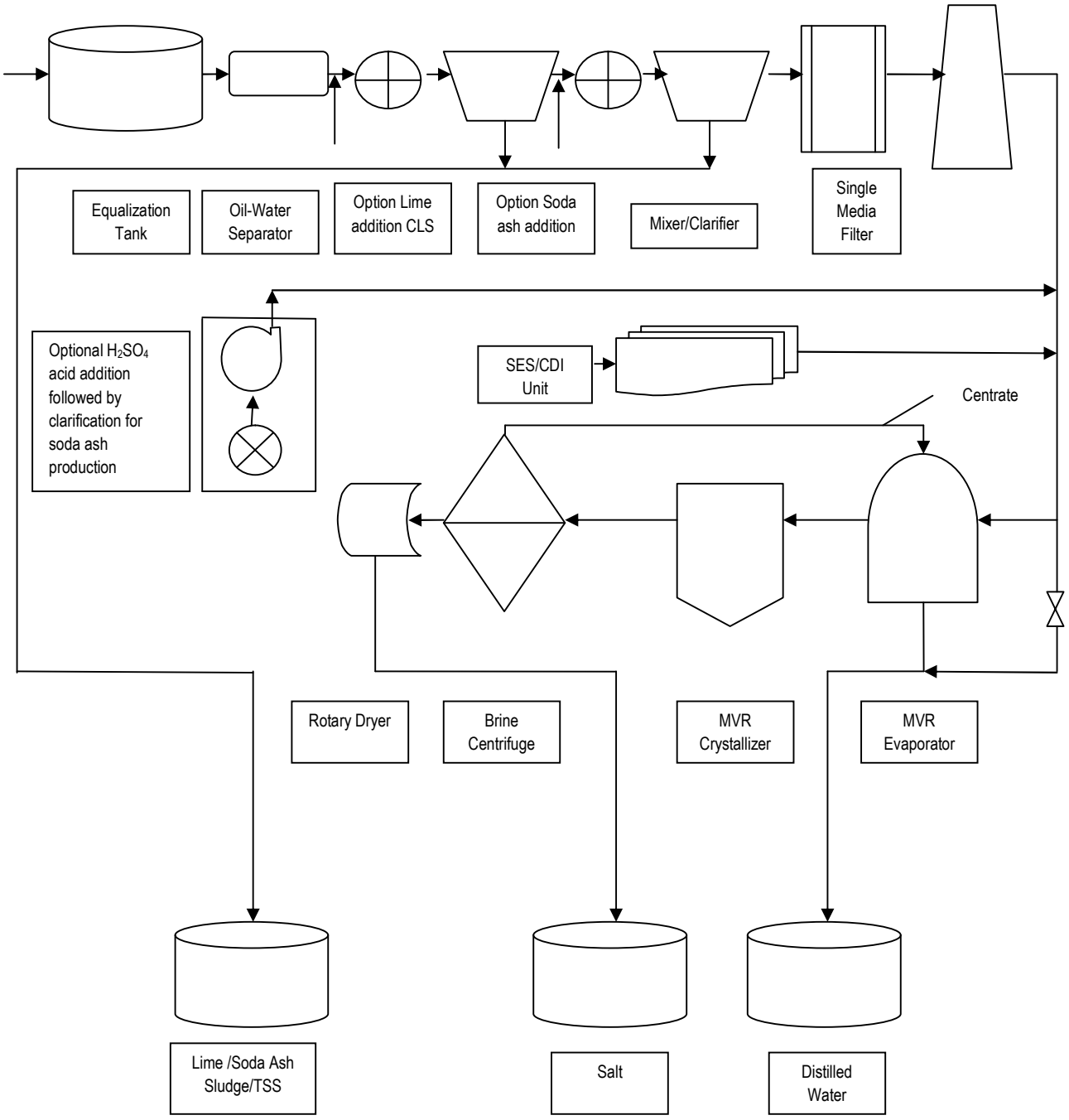
Based on the figure below (Ref. USEPA), the U (VI) distribution coefficient k_d as a function of pH has similar shape for various adsorption media and the highest adsorption value at pH6-7. The affinity of U(VI) to ferrihydrite is higher than that for clay and quartz and is similar to that for activated carbon, carbon aerogels, graphite and graphene which are capable of completely removing the U (VI) oxides and hydroxides.



4. Distribution of U(VI) K_d Values for Sediments and Single-Mineral Phases as a Function of pH in Carbonate-Containing Aqueous Solutions. [Filled circles represent U(VI) K_d values compiled from the literature for sediments, and listed in Table J.5 in EPA (1999b). Open symbols represent K_d maximum and minimum values estimated from uranium adsorption measurements plotted by Waite et al. (1992) for ferrihydrite (open squares), kaolinite (open circles), and quartz (open triangles).]

5. Treatment Process

A general process flow diagram for treatment that entails a uranium/thorium removal unit and evaporation as treatment method for TDS is given below.



6. Summary

The concentration of radionuclides in frac and produced flow back waters (FPW) varies from well to well depending on the physical and chemical composition of the underlying strata and, as such, the levels of radioactivity cannot be accurately predicted. This report defines the average amount of uranium and other alpha particle emitters in FPW based on flow back data for 29 gas wells in Western Pennsylvania. More data is required to define the maximum threshold levels of radioactivity in frac flowback water. Presently, there is no universal radionuclide removal technology that would address all possible variations in concentrations and doses of radionuclides in FPW. Radium 226 and uranium (VI) 238 are the major radionuclides contributing to radioactive drilling rig contamination and waste generation as well as an exponential disposal fee increase.

Besides highly volatile market, the worker's health concern and TENORM and LLRW disposal costs are the major challenges that the O&G operators will be facing in the near future. A long term prospective cohort study is required to address the former. The O&G industry, however, is not ready yet to acknowledge that such an issue exists. In a humble attempt to touch on the latter, this paper lists the most applicable FPW treatment technologies. Physical treatment such as adsorption for uranium and precipitation and co-precipitation for radium and barium were identified as the most flexible and economically feasible methods.

Due to the lack of O&G industry experience with proposed technology applications at such a scale, no Capex or Opex treatment process cost estimates are offered.

7. List of References

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