The Effects of Isotopic Variability on the Gross Detection of Radium in Upstream Petroleum Production Operations

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Sources of Radium in the Petroleum Reservoir

Two elemental radioactive sources of concern in petroleum exploration and production "upstream" operations are naturally occurring uranium and thorium. Both are parents to radium, which has been the element of focus regarding oil field radioactivity. Occurrence of these natural radioisotopes in reservoir rock is much higher in some locales than others in the US and throughout the world (USGS 1999). Potassium has seen far less interest.

Historic Overview

In 1904, J.C. McClellan presented his paper "On the Radioactivity of Mineral Oils and Gases" to the International Electrical Congress in St. Louis, Missouri (IAEA 2003). In 1904 the automobile had not been commercialized on a large scale, and there was widespread belief at that time that radiation doses were healthful, so neither the nascent oil industry nor the rest of the world reacted to McClellan's revelation.

In spite of what is now more than a century of debate, the idea that low level radiation exposures are highly healthful persists (Hotel 2012). Analogous to the issue of the global warming controversy today, the validity of extending the dose response curve linearly to the origin without encountering a threshold, and thus, the actual health effect, be it good or bad, of very low levels of radiation exposure, remains a subject of some debate today (ANS 2012). Part of the controversy stems from the difficulties in how to handle all the variables while mechanically fitting effect to dose, and part stems from a traditional resistance to accepting the idea that alternative biological mechanisms that might operate in response to low radiation dose could be quite different from those mechanisms that are important at high radiation levels, meaning dose-response should *never* be extrapolated downward from high levels. For over a decade, the US Department of Energy has been cosponsoring a reinvestigation that attempts to consider these possibilities (DOE 2010).

By the 1930's, the automobile and oil production was coming into large scale momentum in the Western world, while intentional radioactivity exposure had statistically fallen from grace as a healthful practice conceptually--its fall precipitated by news of the negative effects resulting from very large exposures. Radioactivity from radium coprecipitated in barite was pointed to based on data from Russian oil fields in the 1930's, but again gained little attention. When in 1986, Eddie Fuente with the Mississippi Health Department's Division of Radiological Health advised Street Industries near Laurel, Mississippi, that radiation levels appeared to be of concern in barite scale deposited in tubulars and equipment that Street Industries processed, the service company soon filed suit against Chevron and Shell (Schneider 1990) and after a transition period, the oil and gas industry universally recognized and accounted for the possibility that significant sources of radioactive material might be present in their workplaces. Limitation of company liability through protection of workers and the public from exposure to radioactivity remains the general policy throughout the petroleum industry today.

Discoveries of Variability Within Natural Uranium Isotopic Proportions

The range of uranium isotopic proportions encountered in sandstones or shales typical of a petroleum reservoir may vary less than in igneous rocks, but some significant variation still occurs (Brennecka 2010). The uranium isotopic relative mass fractions in undisturbed rock were once thought to be constant and known to many decimal places, but have in recent years been shown to possess unexpected variability. While outdated, the concept that natural uranium isotopic proportions are well-known and highly fixed can still be seen in many outdated technical documents and are frequently propagated from those sources.

Several theories have been proposed for the variation in isotopic ratio found in natural uranium, but recent research using state-of-the-art instrumentation supports the theory that low-temperature redox changes are the major cause of fractionation between ^{238}U and ^{235}U in many sedimentary formations laid down under low-temperature conditions. Many theories involve alpha-recoil induced solubilization. Accepting latter day values measured for sandstones and black shale deposited in a low temperature redox environment typical of much of the reservoir rock globally, the ^{238}U/^{235}U ratio was shown to vary from 137.848 to 137.918 while the ^{235}U/^{234}U ratio ranged from 136.75to 164.17, a seemingly substantial variation based on high precision measurements (Brennecka 2010). It might be reasonable to question whether this recently acknowledged variation in isotopic fractions should in any way affect the toxicity or handling practices of NORM, since the uranium assay data for petroleum reservoir formations that are not viewed as economically viable sources of uranium could not be expected to be known to any extreme degree of precision. On the same subject of isotopic variability, we might also ask what effect the natural variation in radium isotopes has.

While isotopic ratios have now been shown to vary somewhat in the uranium, the more prolific thorium ore shows negligible variation in nature. Thorium has six naturally-occurring isotopes, but the mass fractions are so small for five that all isotopes can be neglected as components of natural thorium ore other than ^{232}Th, which can be considered mathematically to exclusively constitute all thorium ore found in nature (PTB 2012). Thorium isotopes also occur in the uranium and actinium chains. In reservoir rock that contains any uranium at all, ^{224}Th will obviously be present from ^{238}U decay, ^{231}Th will be present from ^{235}U decay, and ^{230}Th will be present from ^{234}U decay, all of which will vary in concentration with the presence of their parents. Wherever uranium exists, there is a high probability that natural ^{232}Th will also be present, at times exceeding total uranium in mass fraction, and thus its ^{228}Th daughter will be present as well.

Scale Formation

All three natural uranium isotopes decay to thorium isotopes, and most to radium. As a pattern exception, ^{231}Th undergoes beta decay to ^{231}Pa, while ^{224}Th, ^{226}Th and ^{228}Th all decay to their radium daughters. Since radium is a congener of barium these two elements have been shown, as would be expected based on chemical principles, to coprecipitate in piping, tank, and equipment scale. Coprecipitating barium and radium together as sulfates is employed in some of the laboratory procedures for quantifying radium (DOE 1997). Barium sulfate (AKA barite) is a "…dense sulfate mineral that can occur in a variety of rocks, including limestone and sandstone, with a range of accessory minerals, such as quartz, chert, dolomite, calcite, siderite and metal sulfides. Barite is commonly used to add weight to drilling fluid…" (Schlumberger 2012).

In the upstream petroleum industry, the often in situ encountered material known as barite is both a *blessing* as the common well control media of choice to control kicks by quickly overbalancing downhole pressure when its density is added to recirculated mud, and a *curse* when it precipitates in unwanted locations, from tubulars to tanks, pipelines, in gas oil water separators, and even at times in the reservoir rock itself, reducing or destroying the reservoir's porosity and permeability. Barite and other precipitant scale can be extremely hard, can precipitate rapidly over large reaction fronts, and can wreck a producing well in as little as 24 hours after completion. The cost of operational recovery from sudden disastrous scale precipitation can be several million dollars (Crabtree 1999).

When produced formation water is brought to the surface during drilling, or when petroleum product along with produced water are brought up to the production facility together, a series of predictable changes are certain to occur given there is no unusual chemistry interfering, like chelated water, adjusted pH, or anticorrosion constituents such as polymers added. As temperature and pressure drop between formation conditions and the surface world's typical values, barium sulfate ($BaSO_4$), barium radium sulfate [$(Ba,Ra)SO_4$], and at times some calcium carbonate and magnesium carbonate and sometimes several silicates and oxides, may precipitate as scale. As the reservoir ages and pressure drops even more, the precipitation may occur within the producing formation itself. Injection of a poor choice of water can likewise induce precipitation as a reaction front moves through the reservoir rock (Crabtree 1999).

The ratio of ^{228}Ra to the other radium isotopes in oil field scale cannot be calculated from gross measurements or uranium measurements, because no family relationship exists between ^{232}Th and natural uranium. This natural variability is reflected in a USGS report that produced water contains dissolved ^{228}Ra at typically one-half to twice the concentration of ^{226}Ra. Thorium and uranium are frequently collocated in nature, but not in any predictable constant ratio (USGS 1999). One option for examining "average" media in the face of this variability is by employing the Amercan Petroleum Institute's gamma log standard, which was based on a large amount of data and experience. By the late 1950's, more than a generation before Eddie Fuente "discovered" radioactivity at Street Industries, the gamma radioactivity was being measured in about 35,000 wells per year in the US through gamma logging (Belknap 1959). In 1959, it had been known that uranium, potassium, and thorium are generally fine grained and their gamma rays correlate to shale and especially to oil reservoir confinement shale for another generation (since 1940). What was not known, and remains unknown today given that consensus among experts is any indicator, is the real effects of low levels of radiation exposure (DOE 2010).

Changes That Take Place When Radium is Orphaned

Table 1 summarizes the radium isotopes and corresponding sources encountered in upstream petroleum production operations. Researchers from the API subcommittee standardizing the calibration of nuclear logs examined data from over 200 shales and concluded that the average shale contains approximately 6 ppm uranium (^{238}U), 12 ppm thorium (^{232}Th), and 2 percent potassium (Belknap 1959). The potassium referred to is K-natural, not K-40 (API Subcommittee 2002). The gamma log calibration standard at the University of Houston is double these concentrations by design (Belknap 1959). This API standard remains an accepted calibration model for wire-line gamma logs, with a variety of corrections made for casing, pipe, mud, especially KCl and barite, tool speed, geometry, and several other factors depending on whether the log is wire line or log-as-you-go and on the details of data acquisition.

Table 1: Radium at the Instant of Separation by Coprecipitation in Mud, Sludge, Piping, and Equipment With Barium Sulfate

Source	Radium	Half Life	Unit	Normalized Activity
^{238}U	^{226}Ra	1600	Years	42.5%
^{235}U	^{223}Ra	11	Days	1.9%
^{232}Th	^{228}Ra	5.8	Years	27.8%
^{232}Th	^{224}Ra	3.7	Days	27.8%

The normalized radioactivity shown in Table 1 is based on the uranium to thorium ratio derived for representative shale during derivation of the original gamma log standard (Belknap 1959) coupled with the highest fraction for ^{235}U provided in the mass fraction study discussed previously (Brennecka 2010). With the long accepted "average" uranium isotopic ratios, the ^{226}Ra would be very slightly larger and the ^{223}Ra would be very slightly smaller. At the point of fluid production, the four isotopes in Table 1 brought up to the surface will be forever "orphaned" or separated from their uranium and thorium parents as they continue their natural decay chains as orphaned parents themselves.

Radioactive decay has long been known to occur as a first order function--at a constant rate of change:

$$\frac{dN}{dt} = -\lambda N$$

where N is the number of atoms or units of mass
t is time
and λ is a rate constant in decays per unit of time.

More importantly to the radium discussed here, we can extend this “constant rate of decay” pattern to write a linear first order differential equation that describes a general universal parent-daughter relationship as follows:

$$\frac{dN_d}{dt} = -\lambda_d N_d + \lambda_p N_p$$

where N_d is the number of atoms or units of mass of daughter
N_p is the number of atoms or units of mass of parent
t is time
λ_d is the rate constant for the daughter
and λ_p is the rate constant for the parent.

The most general and useful solution to this taken from time 0 to t is:

$$A_d(t) = A_p(0)\frac{\lambda_d}{\lambda_d - \lambda_p}(e^{-\lambda pt} - e^{-\lambda_d t}) + A_d(0)e^{-\lambda_d t}$$

This is often called the “daughter equation” or the general Bateman equation. Several other solutions are frequently employed based on case-by-case boundary conditions that can be applied, such as the relative decay rates of parent to daughter, but since a calculator or computer will almost always be used for calculating antilogs, and since antilogs are in every possible solution regardless of boundary conditions, no other equations are really needed to predict the radium-orphaning results of drilling or petroleum production. The daughter equation is a popular choice that reduces error.

The beauty of the daughter equation is that this equation is equally useful for moving through several generations of isotopes at once, after equilibria have been established that apply to these chains, which in many cases occurs very quickly. The daughter equation, along with its right hand term alone as the decay equation, can be applied to the four radiums that are always present in freshly separated NORM, to see what happens when we orphan them as parents. One thing we see is that in a little over a month, the common radon gas ^{222}Ra reaches the same decay rate of its parent in the common decay relationship called secular equilibrium.

While numerically you might see this taking around 43 days when the convergence is calculated out to several decimal places, we can see from the plot in Figure 1 that most of the radon is already grown in within a week. Radon gas is fairly soluble in aqueous solutions and tends to stay in wet substrates, like freshly deposited wet precipitates--the importance being that wherever the radon ends up, the rest of the chain will be produced there as well by subsequent decay. This causes polonium and lead deposits in gas equipment, a subject not examined here. From the daughter equation, we can also see that in a month or two, ^{223}Ra and ^{224}Ra will disappear forever as shown in Figure 2.

Figure 1: ^{222}Ra Reaching Secular Equilibrium with its Parent after Separation, per the General Daughter Equation

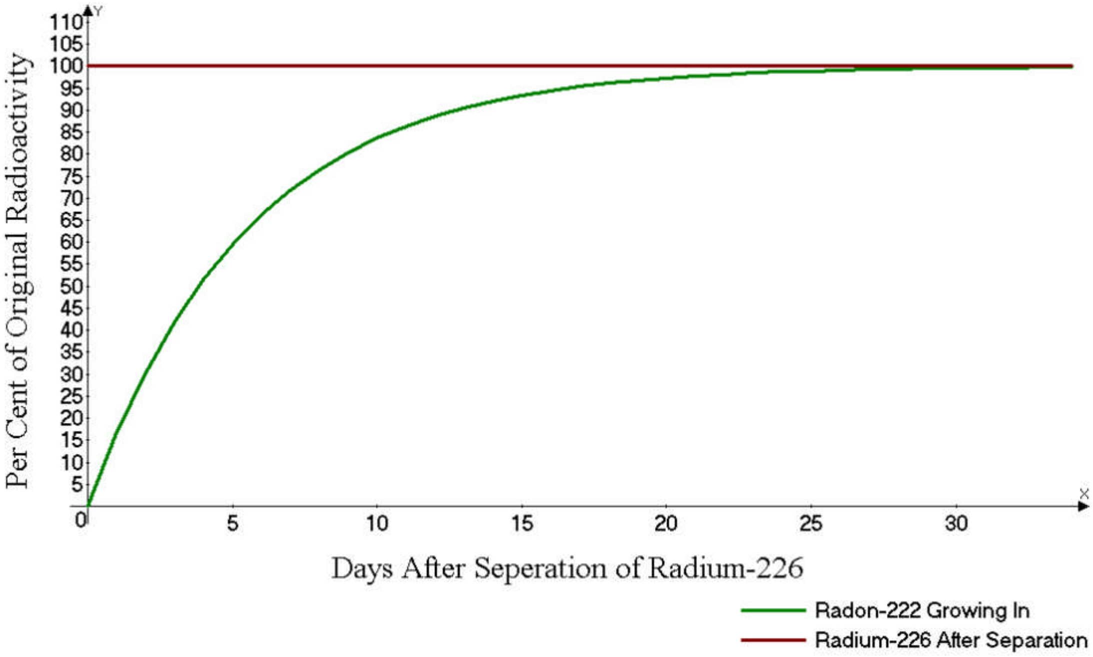
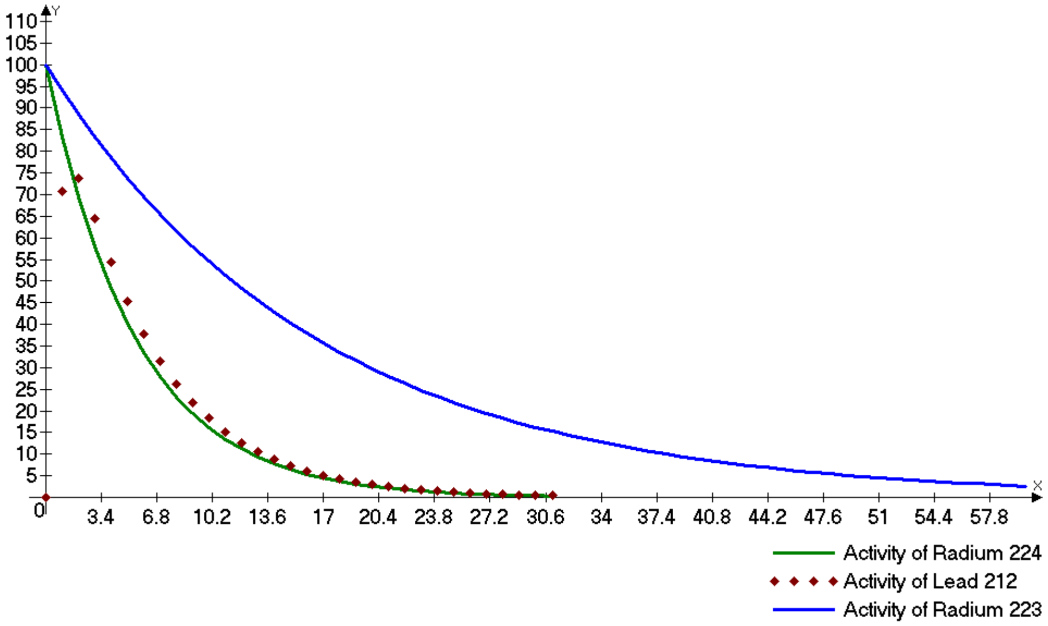


Figure 2: ^{224}Ra and ^{223}Ra Decay Away Quickly After Separation



These early changes affect the source of exposure. Using MicroShield 6.02 for point source modeling at 10 cm (4.94 inches), a comparison was made for where the gamma exposure arises at the time barium radium sulfate [$(Ba,Ra)SO_4$] is precipitated on piping and equipment, in mud, or wherever it happens. MicroShield is now available at Version 9.XX in 2012 with many improved features (Grove 2012). Figure 3 illustrates where gamma exposure originates for freshly precipitated material if we assume the API gamma log standard isotopic ratios. Note that most of it is coming from ^{228}Ra, which turns out to very weak x-rays to be discussed later.

Figure 3 assumes radium precipitates alone without daughters or parents, which is generally the case based on chemistry. Since Figures 3 and 4 rely on normalizing exposure rates to examine only the relative isotopic contribution, exposure has no units. Upon precipitation, the ^{228}Ra daughter of ^{232}Th appears to be the largest contributor to external gamma, but these are not very energetic gammas. Decaying the radium isotopes for ten years and repeating the MicroShield modeling, we see the total gamma exposure grow by a factor of 22. Plotting the normalized exposure rates again as Figure 4, we see that ^{226}Ra has become the larger source and the short-lived ^{223}Ra and ^{224}Ra are of course long gone. Exposure in Figure 4 has no units, but real world exposure rates are typically very low--in the µr to tens of µr/hr range near production piping and equipment. Some points for daughter ^{212}Pb are shown in the figure because it is the slowest decay rate daughter so its ingrowth rate time might be of interest. The others will cascade to secular equilibria along the chain of decay very rapidly, per the daughter equation.

Of course neither Figure 3 nor 4 illustrate even an idealized oil and gas production facility, which might have both aged scale and newly deposited precipitate together. The typical case given the API standard reservoir rock would be between the two and weighted temporally toward Figure 4. Precipitation scaling can be sudden and prolific, slow and steady, or any combination. Caliper logs have shown scaling rates like 0.1” per month while precipitation fronts can also shut down a well completely overnight (Crabtree 1999). Fresh radium could be added at any instant during drilling, workover, or changing operations.

In Figure 4, we see that ^{226}Ra dominates the activity, which is what has always been thought, so the varying isotopic fractions in natural uranium have no consequential effect on NORM practices. What the newly promoted higher fraction of ^{234}U does is to slightly increase the ^{223}Ra fraction shown in Table 1, after which this chain quickly expires with no interesting effect.

The natural variation between ^{232}Th and ^{238}U is far greater than the variation within the natural uranium isotopes, but before examining the radium ratio variants in natural reservoir rock vs. the API standard, other natural isotopes that could be encountered by upstream production workers are briefly discussed, along with how these isotopes could be exposed.

Figure 3: Typical Normalized Exposure Contributed by Radium Isotopes

Upon Precipitation of Radium

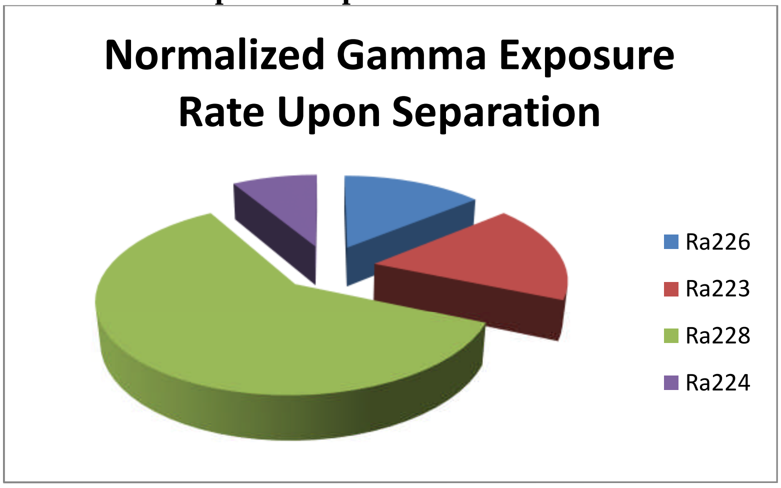
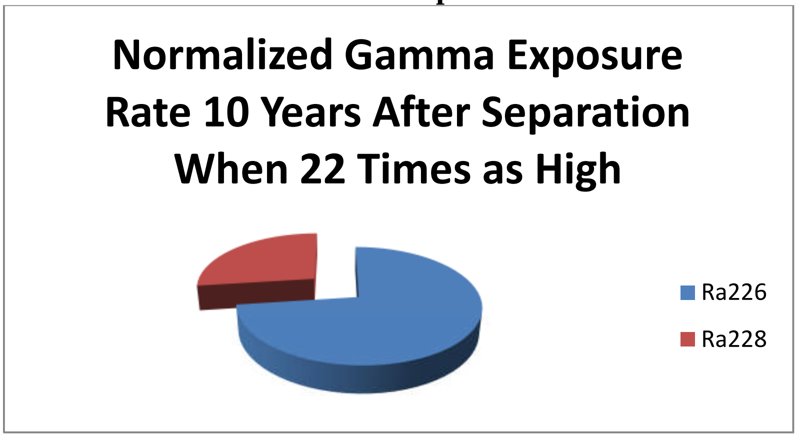


Figure 4: Typical Normalized Exposure from Radium Isotopes 10 Years After the Precipitation of Radium



Potential Isotopes Other Than Radium

Obviously the cuttings from any reservoir shales or sandstones high in radium will contain the natural uranium and thorium parents as well. Keep in mind that these are typically at low concentrations and in limited volume. Operational processes would be expected to sequester other isotopes into production. If scale inhibitors are used to reduce scale buildup, then tank sludge can be more concentrated in specific isotopes (Bradley 1996). Removing scale mobilizes and relocates the radium, ideally back to an acceptable receiving formation for produced water, and in many cases often viewed as the ideal, to the originating strata via injection wells.

Scale can be dissolved or controlled by the use of acids, which are also used in several enhanced recovery schemes. The conventional preflush technique of standard enhanced recovery involves pumping hydrochloric acid ahead of the main treating fluid. The main fluid is a mixture of hydrofluoric and hydrochloric or organic acids for a sandstone matrix-stimulation treatment. (Schlumberger b 2012). Formic acid may be preferred to hydrochloric for its superior corrosion removal and corrosion-control properties (Schlumberger c 2012). Fifteen per cent hydrochloric is often used as part of the fracturing process in gas shales (Shein 2008, Arthur 2011). Phosphoric acid may provide synergistic enhancement to hydrochloric alone (DOE 2005). Acetic, sulfamic, or chloroacetic, are also commonly used in addition to formic, hydrofloric, hydrochloric, phosphoric, and various acid blends (Cleansorb 2006).

The solubility of uranium, thorium, and potassium are significantly increased by the addition of acids, which is why solution mining is a popular process for intentionally bringing concentrated uranium up in wells. About 26% of all uranium production globally is through in situ leach mining of uranium by using acid (World Nuclear, 2010). Obviously, when acids are used in the reservoir, more isotopes than radium could at times be produced in the recovered fluids.

When scales form that compromise or halt entirely production operations, a progression of responses are sometimes made if initial efforts fail. Inorganic acids effective on carbonates do not work well on all sulfates. Granular media blasting effective on halite is not very effective on hard barite scale. (Crabtree 1999). Chelators are popular and work well on carbonate and at times on other species (Crabtree 1999, Dietz 2008). Many scale inhibitors are based on phosphates or organic polymers. Thermodynamic inhibitors are complexing and chelating agents, suitable for specific scales. Scale inhibitors for barium sulfate include ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) (Dietz 2008). These are the same chelators shown to chelate uranium and thorium in soil washing (Devgun 1993) so any treatment involving uranium- and thorium-bearing reservoir rock could potentially result in chelated parent isotopes produced in the fluids and holding ponds.

As deposited radium is removed from the well bore, piping, tanks, and equipment, it is expected that other metal cations, especially potassium in large quantities, will be added to fraccing flowback and to routine reservoir produced water. In cases where injection into disposal wells is not practical and water treatment is performed prior to discharge, raising the pH as well as other treatment process may result in nuclide concentration based on the physicochemical parameters. With the increasing promulgation of NORM regulations by the states, use of potassium choride and other potassium rich products in production, and the prolific availability of potassium in nature, this could at times pose a regulatory issue, because some NORM disposal regulations are set near naturally occurring potassium peak levels (i.e., 35 pCi/g). Some NORM regulations make an exception in recognition of high natural potassium while others do not differentiate, and an exception should always be made.

Although radium has attracted the most historic attention because of its precipitation in oil field scale with barium and calcium, if radium is present in the revervoir rock, its parents and daughters are also present. To the extent that they are brought up in produced water and then returned via injection wells and remain in solution during their surface stay, there is no real safety issue. Again taking the “standard” radionuclide content of shale as determined by the API subcommittee

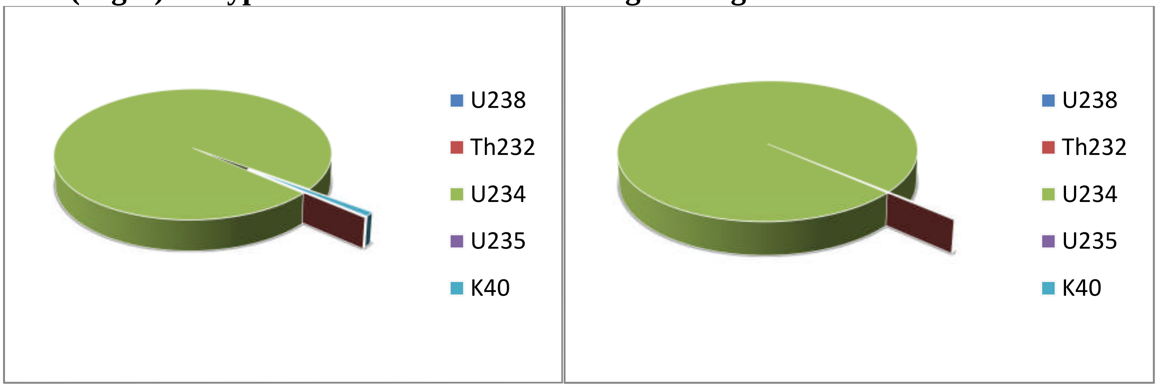
(API 2002) and the "high" ^{234}U fraction (Brennecka 2010), data for the right-hand graph of Figure 5 was produced by MicroShield runs (with the chains in secular equilibrium), and is highly correlated to radioactivity on the left hand pie. ^{226}Ra is in the ^{234}U and ^{238}U chains, but ^{234}U is decaying much faster than ^{238}U as ^{238}U feeds it. Switching to the "low" ^{234}U fraction in the new data produces no visually perceptible difference when the left hand and lower pie charts are compared, showing that the trends in relative hazard are imperceptibly affected by isotopic variation in natural uranium.

The Effectiveness of Routine Direct Radiation Exposure Surveys

Presumably, routine workplace surveys would employ common Geiger-Mueller (GM) ratemeters and (or) micro-R sodium iodide (NaI) scintillation ratemeters, with the latter being more sensitive at the low levels that would be expected at many well sites, but possibly going off-scale from some thicker scale buildups and mandating a switch to a GM detector. If isotopes suddenly change during acid use or as new formations are encountered during drilling, there could be concern over whether instrument calibration is appropriate. After all, these ratemeter instruments provide gross readings that do not differentiate between isotopes. Figure 6, approximated from Ludlum Instrument's Model 19 MicroR/Ratemeter specifications (Ludlum 2012) illustrates the energy dependency of the Model 19's efficiency. The Model 19 is perhaps the most popular micro-R range ratemeter scintillator for direct exposure surveys, because it detects very low levels of gamma that are more commonly encountered in the upstream production work areas. The energy response, however, is not as good or as broad for micro-R NaI scintillators as for most GM detectors. Ratemeters with GM tube detectors will show an even better energy response and to a lower energy range and in higher energy regions, the only problem being that they will not detect well down in the very low abundance range of tens of μr/hr typical of production facilities, so the combination of GM and micro-R are both valuable and best used to augment each other.

As evident from Figure 7, which plots the decay gammas for the radium distribution shown in Table 1 after aging 5 days for daughter ingrowth, the micro-R is highly capable of detecting this material. It tends to overstate radiation levels at energies around 100 to 500 keV, which is needed due to the sparse abundance of decays there, and it still detects the points to the right of the red square with some diminished efficiency. Given the API isotopic ratios again, in considering how well freshly separated radium is detected upon bringing up precipitate or fluids, see Figure 8, which depicts freshly precipitated daughterless radium. The micro-R has at least some detection capability on all isolated Ra isotopes except ^{228}Ra. It cannot detect ^{228}Ra at all for the first hours after separation from its parents and daughters because it decays with an alpha and in 100% of the decays, a weak 0.0067 MeV x-ray that is below the threshold of detection for that instrument. Essentially, ^{228}Ra has no genuine gamma signal until daughters have ingrown for a while. The only hope of detecting this x-ray with a Micro-R would be based on secondary radiation buildup in the casing housing the sodium iodide. The buildup factors for low-energy "soft" x-rays in this region have been increased as a result of modeling about ten years ago, and while outside the scope here, significant detection of 6.7 keV x-rays with most micro-R style ratemeters will be dismissed as highly unlikely, since the soft x-ray would not even be expected to penetrate the robust aluminum housings employed for most designs of these rugged field instruments. Other manufacturers produce micro-R range devices and details will vary.

Figure 5: ^{234}U Dominates Activity (Left) and Normalized Gamma Exposure Rate (Right) in Typical Reservoir Shales Having the Highest ^{234}U Found in Nature



^{234}U Dominates Activity (below) with Negligible Apparent Difference in Typical Reservoir Shales Having the Lowest ^{234}U Found in Nature

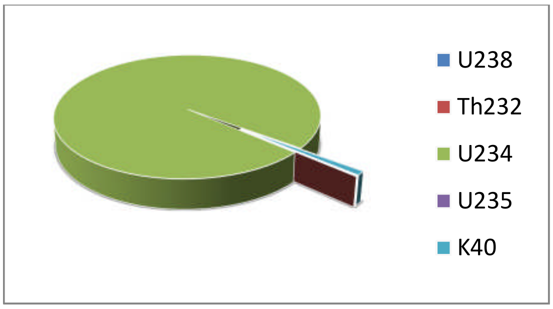


Figure 6: Energy Response Curve for the Ludlum Micro-R

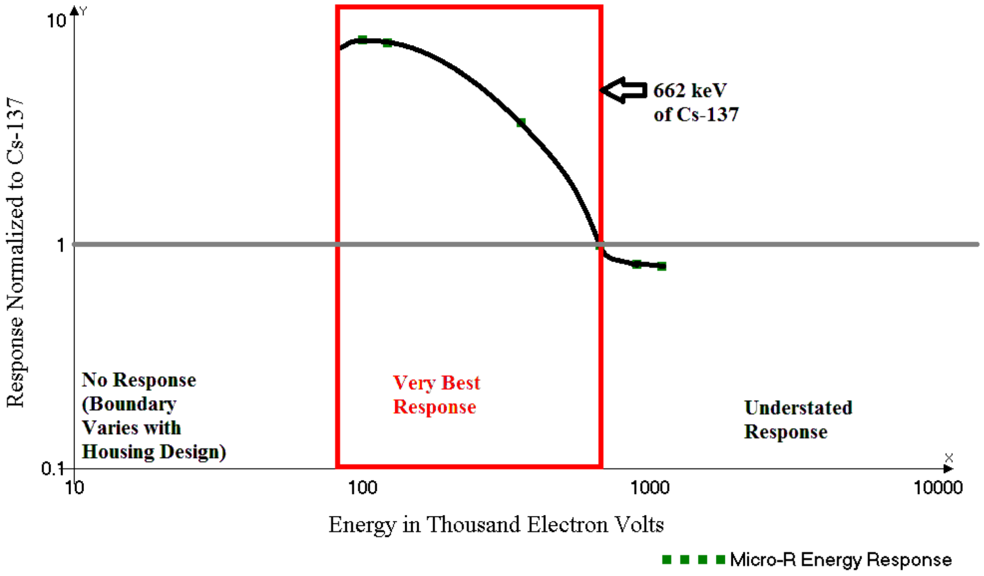


Figure 7: Per Cent of Energy Activity
Vs. Energy Per Emission From 5-Day Old Radium Scale

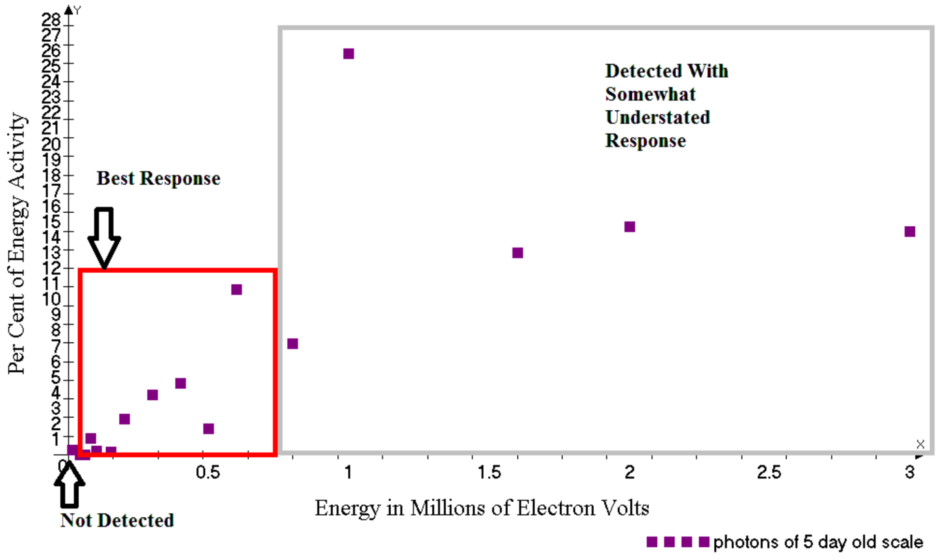
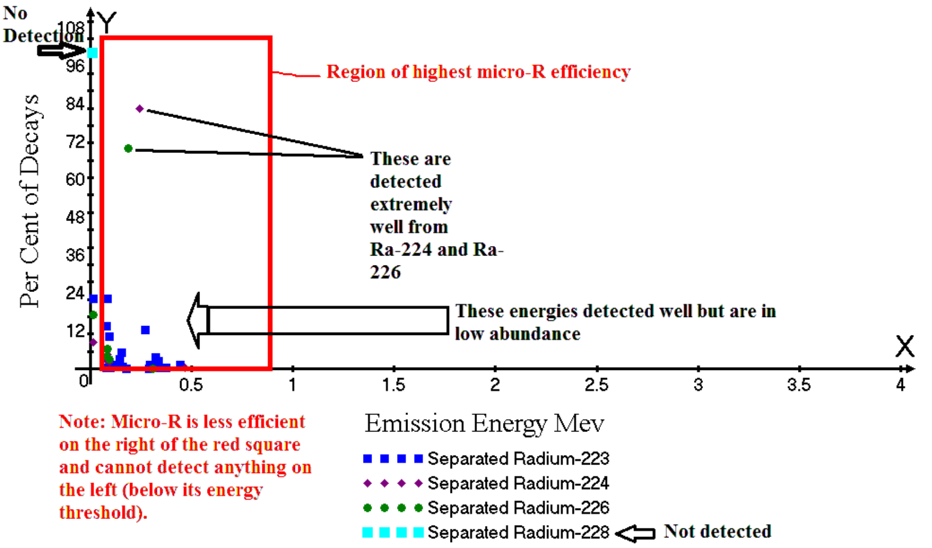


Figure 8: Per Cent of Decays of Freshly Precipitated Radium
Prior to Daughter Ingrowth vs. Emission Energy



There are really two cases worth mentioning about the red squares highlighting the “best” energy response zones. In the figures, lower energies (points shown *left* of the red squares) cannot penetrate the detector’s shielding at all, so no signal whatsoever is created, while higher energies (points right of the red square) tend to pass through the vacuum in space between the standing waves of condensed matter in the sodium iodide crystal without interaction much of the time, due to the limited size of the crystal and the gamma wavelength. Some fraction of the high energy photons do interact, so some signals result, albeit at lower efficiency than within the ideal energies found inside the red square. A phenomenon worth considering that is posed by the inadvertent chemical separation of radium from its parents in the petroleum production process is that the presence and location of radium is hard to see in freshly precipitated scale with the field ratemeters, while a dose potential is presented if inhalation or ingestion of this fresh material takes place. Lower ^{228}Ra:^{226}Ra material will be less understated sooner after precipitation. The range of ^{228}Ra:^{226}Ra ratios in different reservoirs will be discussed later.

Ingestion and Inhalation

Since we have shown that for API gamma log standard reservoir rock, freshly precipitated ^{228}Ra is not detectable with a micro-R meter, we might ask hypothetically, how much ^{228}Ra could be ingested on say, a contaminated sandwich and not exceed the annual occupational dose limits of 5 Rem for nuclear industry workers shown in Table 2. The annual level of ingestion corresponding to 5 Rem is 2 μCi per the NRC in 10CFR20 Appendix B Table 1 (NRC 2012), so at a specific gravity of 2.5 and the highest concentration reported in scale of 0.4 μCi/g, you would need to ingest 2 cc of scale to represent the annual maximum dose limit, which is not a credible mistake taken as a solitary ingestion event. Two cc of scale is a fair amount of material and a 2 cc sample makes a training illustration people can easily relate to. For median concentrations, a 4 cc sample is needed and for arithmetic average radium-contaminated scale, a very *very* large sample.

Table 2: Allowable Intakes Equating to 5 Rem for Occupational Radiological Workers

Isotope➔	^{223}Ra	^{224}Ra	^{226}Ra	^{228}Ra
Oral Ingestion	5.0 μCi	8.0 μCi	2.0 μCi	2.0 μCi
Inhalation	0.7 μCi	2.0 μCi	0.6 μCi	1.0 μCi

Of course pure reduced radium metal never preciptates as scale. Common scale may consist of barium sulfate, calcium carbonate, gypsum, other sulfates, iron carbonate, iron oxides, iron sulfides, and magnesium salts (Dietz 2008) and strontium sulfate (Crabtree 1999). Scale radium activity concentrations have been reported to peak at about 0.4 μCi/g (EPA 1993, Smith 1998, USGS 1999) so 2 cc of pipe or tank scale of the worst scale reported could be ingested over a year without exceeding the allowable nuclear-industry dose maximum to a worker.

Of course inhalation is a much more likely hazard than ingestion, and the threat of inhalation by the public is a good reason to plastic wrap or otherwise contain tubulars and equipment moved over public roadways between workover sites, since road traffic could take scattered dropped material airborne (Swan 2004). The risk of inhalation by workers is a reason to work with wet material when possible. Inhalation control and a reliable airborne radioactivity management and respiratory protection program is a complex subject unto itself so that discussion is deferred here.

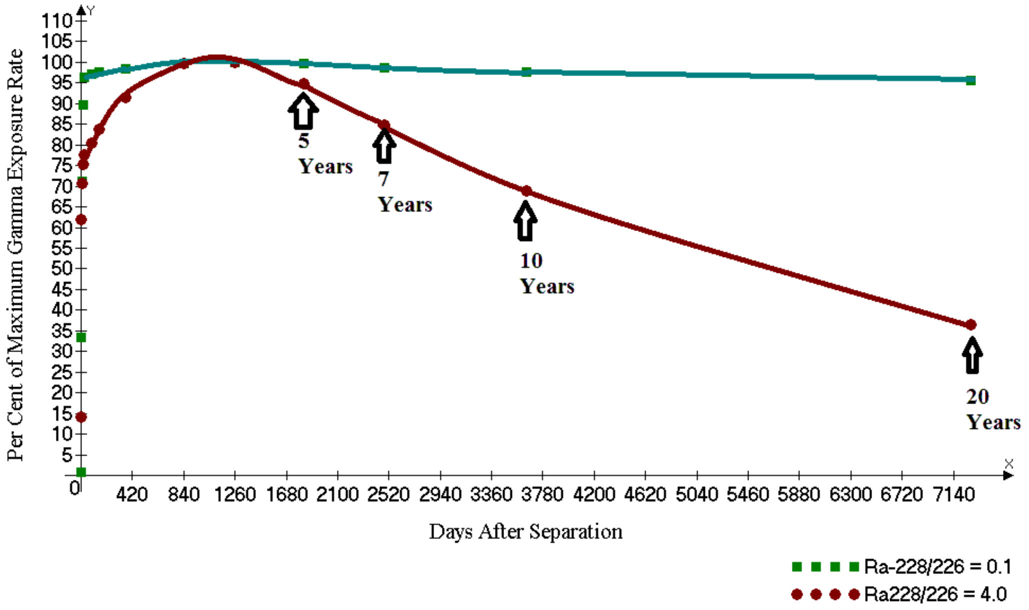
The critical importance of a good radiation protection program is to control company liability, because detection of an unacceptable radium body burden in a worker through bioassay tests would present an unacceptable and easily avoidable risk of litigation. During the time while freshly precipitated radium is more difficult to detect before the daughters have ingrown, the internal hazard remains the same. Without appropriate contamination control practices, inhalation and ingestion of radium could be overlooked. Considering that ^{228}Ra rarely occurs without other Ra in nature, and that others would normally be expected in fresh precipitant and that daughters will grow in quickly, isolated ^{228}Ra appears unrealistic in real world operations. The gamma abundance from the other radium isotopes is also relatively weak immediately after precipitation, so until daughters grow in, radium is generally more difficult to detect in any freshly separated scale. As soon as there is appreciable ^{228}Ac grown in, ^{228}Ra will be well represented in micro-R measurements, which will be in a few hours and ^{228}Ac will grow in completely the second day. It is ^{208}Tl that will continue strong gamma growth beyond that, growing with its ^{228}Th ancestor. Using the daughter equation we see that it will take a little over a month to grow in 1/3 of the ^{228}Th daughter that controls all lower chain members (because of their very high decay rates).

The Effect of Variability in the ^{228}Ra to ^{226}Ra Isotopic Ratio on Gamma Exposure Rates

All the discussion to this point centered around reservoir rock that has the API gamma log standard isotopic ratios. In reality, there is substantial variability in these ratios in nature. As noted previously, this variability is reflected in USGS report that produced water contains dissolved ^{228}Ra at typically one-half to twice the concentration of ^{226}Ra. Researchers found ^{228}Ra and ^{226}Ra isotopes appear to be only moderately correlated ($r = 0.63$) in Mississippi oilfield NORM as compared to a very strong correlation ($r = 0.98$) previously seen in Texas wells (Swan 2004). In another comparison, samples from produced water from the Marcellus Shale were usually less than 0.3 ^{228}Ra to ^{226}Ra activity per mass, while samples from non-Marcellus reservoirs were usually greater than 1, with 1.6 being the standard value for sandstone reservoirs globally (Rowan 2011). A researcher of Syrian data found a 0.76 ^{228}Ra to ^{226}Ra activity per mass ratio there (Al-Masri 2005). Samples from sludge and scale in Brazil varied from 0.53 to 2.7 while averaging 0.9 ^{228}Ra to ^{226}Ra activity per mass (Gazineu 2012). Overall, newer information continues to support USGS' report of an order of magnitude variation reported between ^{228}Ra and ^{226}Ra activity per unit mass in radium from reservoirs. The ^{228}Ra to ^{226}Ra ratio is more of a variability of interest than the uranium mass fractions, because it is significant enough to matter, and is caused by the variability of ^{232}Th to ^{238}U in reservoir formations.

To examine the effect of isotopic ratio variability on exposure, a low ratio of 0.1 ^{228}Ra to ^{226}Ra activity per mass was selected from the Upper Ordivician Queenston Shale data and a high of 4.0 from the Lower Silurian Medina/Tuscarora Sandstone, both presented by Rowan (Rowan 2011). Most radium in oil field NORM should fit within the range between these two values found in nature. Normalized exposure as modeled previously for the API gamma log standard ratios was plotted in Figure 9 comparing these two real measured extremes. It is evident from the plot that both cases grow exposure rate in quickly once separation from the parent nuclides occurs, both peaking in exposure rate at about three and a half years and then gradually declining, with the ^{228}Ra dominated sandstone material declining much more rapidly because of the relatively shorter ^{228}Ra half-life. Note how much exposure rates will grow from scale with similar isotopic fractions to the sandstone until the peak is reached.

Figure 9: Effect of ^{228}Ra to ^{226}Ra Ratio on Gamma Exposure Rate Over Time



Conclusions and Observations

- The recently accepted substantial variability in isotopic fractions in natural uranium has no effect on safe practices in the work place regarding NORM. ^{226}Ra dominates long term as ^{228}Ra is lost to decay. When it exists in nature, slightly higher ^{234}U produces proportionately more ^{226}Ra, which is commonly already dominant. Slightly higher ^{235}U produces more ^{223}Ra which quickly disappears with no impact. In summary, the uranium isotopic variability recognized in recent time is of no concern.

- The naturally occurring ^{232}Th to ^{238}U ratio is what determines the ^{228}Ra to ^{226}Ra ratio and will affect how long the radioactivity in waste and old scale contamination could pose a hazard, so this is the real variability that appears to be significant insofar as radium in oil field NORM. For injection wells it may be of no consequence, but this ratio could matter when looking at things like the long term impact of land application of radium scale and sludge, as obvious for Figure 9, which is based on actual reservoir rock.

- Micro-R type sodium iodide scintillation detector rate meters calibrated to the ^{137}Cs gamma are appropriate for the emission energies encountered in oil field NORM. Freshly separated ^{228}Ra may be “invisible” to the field ratemeters. The higher the ^{228}Ra to ^{226}Ra ratio the more difficult fresh radium-containing precipitant will be to detect with hand-held gross ratemeters. All scale will be much harder to detect immediately after separation from the parent and daughter material, but so long as there are good radiation protection practices against ingestion and inhalation of NORM contaminants, workers are adequately protected. Personnel should always be conscious of the diminished ratemeter detectability in fresh precipitant. Material that did not appear to be radioactive yesterday could be quite detectable tomorrow.

Conclusions and Observations (continued)

- We should anticipate the possibility of isotopes other than radium, such as uranium and thorium parents, to be produced in fluids when acidification, chelation, and other chemical treatments are used that would obviously interact with light metal and actinide species when these are known to be present in a reservoir. As long as these remain in solution and are reinjected in wells, they would not significantly affect the contaminant profile of the site.

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