Optimized Geochemical Modeling of Produced Fluids Provides Important Insight into NORM-Related Issues

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Oil and Gas Processing Waste is only One of the Types of NORM Wastes Recognized by the EPA

Aluminum Processing Waste
Coal and Coal Ash Waste
Consumer Products
Copper Processing Waste
Drinking Water Treatment Waste
Fertilizer Waste
Geothermal Waste
Gold and Silver Processing Waste
Oil and Gas Processing Waste
Rare Earth Processing Waste
Tin Processing Waste
Titanium Processing Waste
Wastewater Processing Waste
Zircon Processing Waste

Approximately 100 tons of scale per oil well is generated annually in the United States.

The average radium concentration in scale is estimated at 18 Bq/g. It can be as high as 14.8 kgBq/g.

Additional information may be found at the U. S. EPA TENORM website

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NORM Contamination Related to Oil and Gas Production has been Known for Decades

1904 - NORM is found in oilfield hydrocarbons

1951 – NORM-bearing scale and sludges in pipes and production equipment

Millions of barrels of petroleum-related NORM awaiting disposal

150,000 barrels being generated per year

American Petroleum Institute in 1989 suggested that 1/3 of all producing U.S. oil and gas wells have elevated radiation

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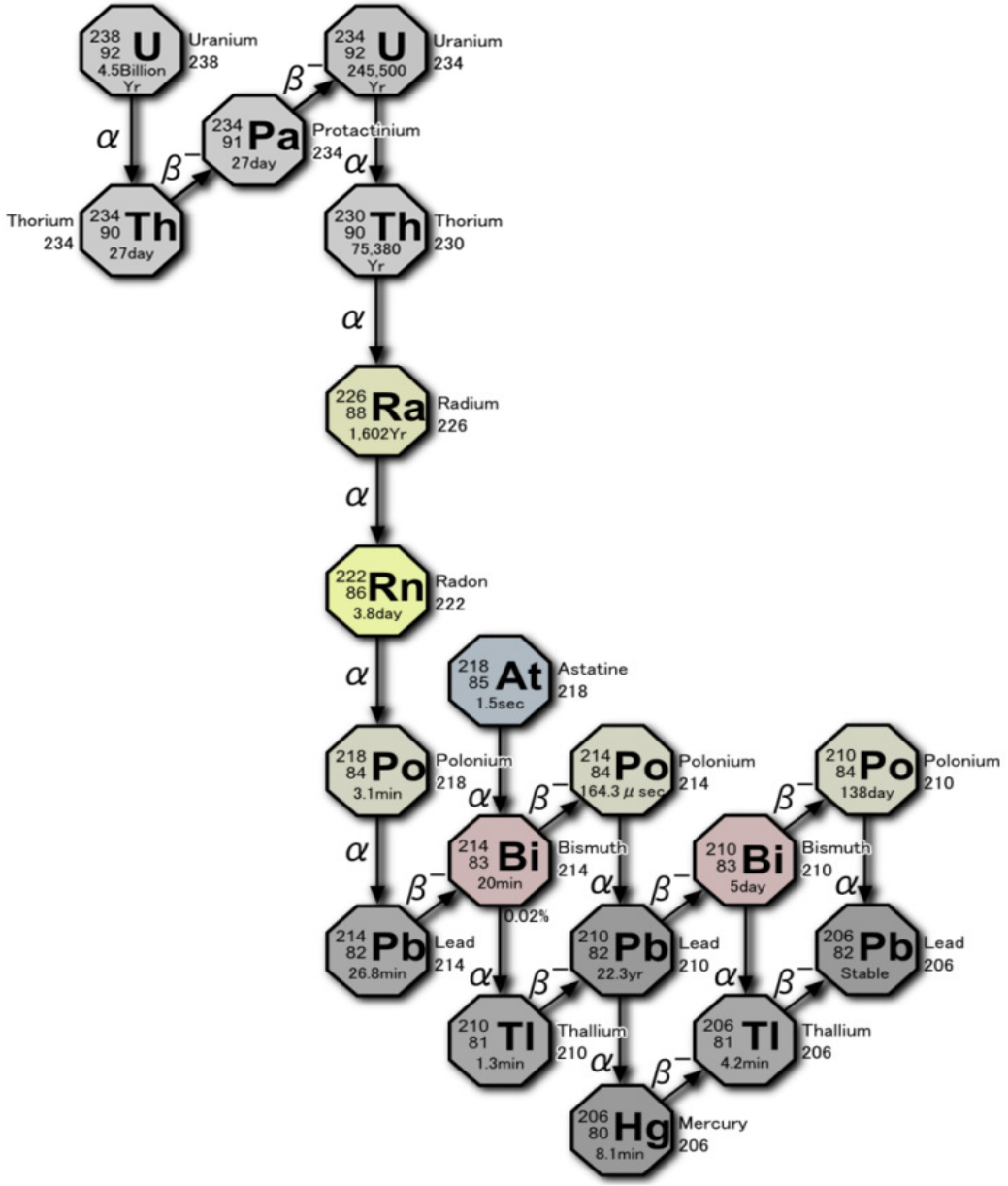
Radium and Radon are the Primary Uranium Decay Products of Interest

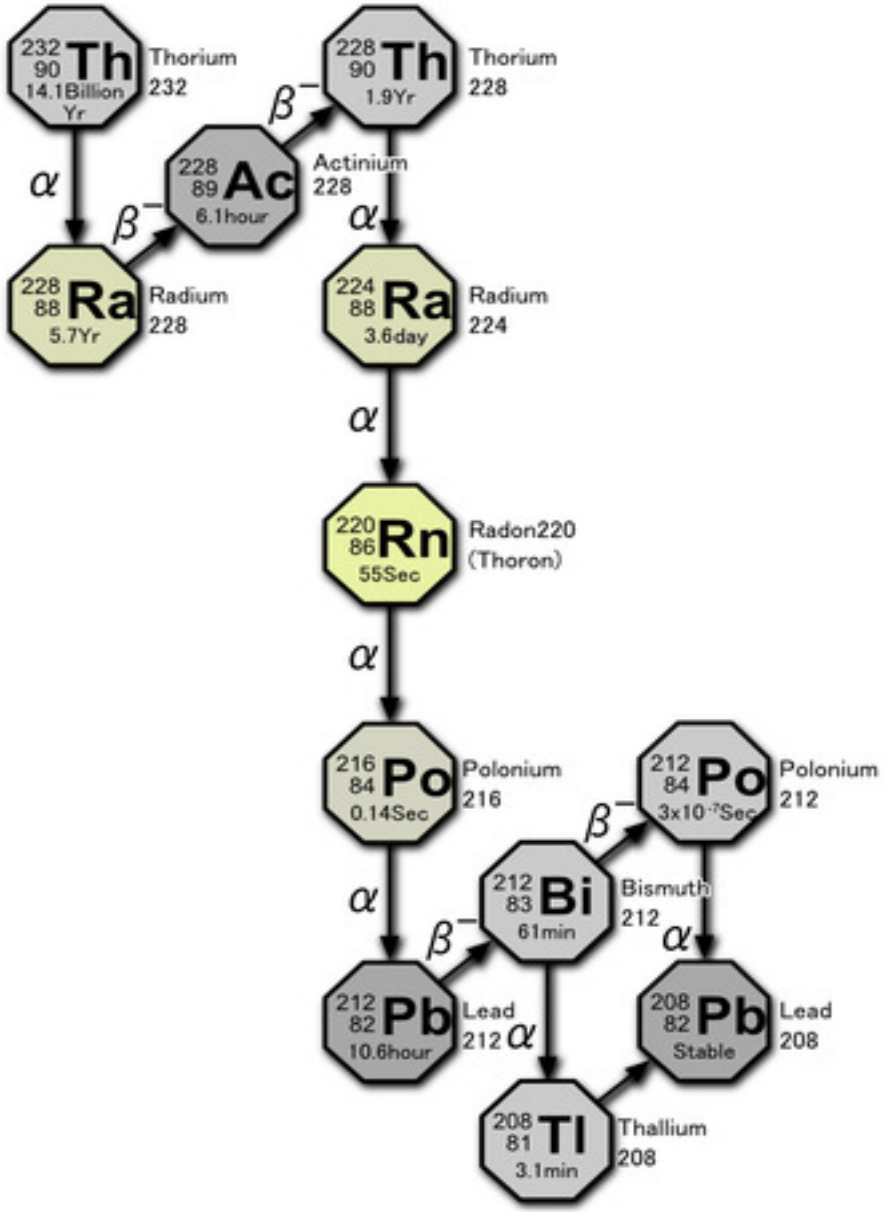


Radium is chemically similar to calcium - "bone seeker"

Radon is an inhalable gas and can cause lung cancer

Unique Geochemical Behavior for each Radionuclide

Radium and Radon are also Produced within the Thorium-232 Decay Chain



Separation by geochemical processes of the thorium parent from the radium daughters results in rapid deletion of the radium due to their short half-lives

Only about 6% of initial Ra-228 remains after about 25 years (4 half-lives)

Ra-228 therefore is typically not a radionuclide of concern at legacy operations

Precipitation of Alkaline Earth Sulfates May Co-Precipitate Radium Sulfate

$$Ba^{+2} + SO_4^{-2} \rightarrow BaSO_4$$

$$Ba^{+2} + (Ra^{+2}) + SO_4^{-2} \rightarrow Ba(Ra)SO_4$$

Acid Insoluble
Readily Pass TCLP for Barium
Physically Resistant Scale
Dense – Hard to Physically Wash Out
Dominantly Physical versus Chemical Dispersal

Addition of Barium Chloride [$BaCl_2$] (a soluble form of barium) and Sodium Sulfate [Na_2SO_4] results in the removal of dissolved radium from solution – Proven wastewater treatment process

Radium can also Co-precipitate with Calcium and Strontium

$Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 * 2H_2O$

$Ca^{+2} + (Ra^{+2}) + SO_4^{-2} + 2H_2O \rightarrow Ca(Ra)SO_4 * 2H_2O$

$Ca^{+2} + (Ra^{+2}) + SO_4^{-2} \rightarrow Ca(Ra)SO_4$

Acid Soluble – HCl
Less adherence of the scale
More readily removed
Potential release of radium

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Geochemical Modeling Provides Insight into Radium Activity and NORM Formation Potential

Fixed rate of radium generation (and decay) from oil field host rock

Assumption of "Secular Equilibrium" – radium activity in a steady state (safe assumption)

Radium activity is dependent on:

- Uranium concentration – 3 milligrams per kilogram
- Porosity of Rock – 20%
- Brine Density – 1.35 grams per liter
- Radium Transfer to Brine Phase – ?

At 100% transfer efficiency Ra-226 concentration in brine – 26 ppt (parts per trillion) or 960 Bq/L

Empirical measurements document 55 Bq/L (1.3 ppt) as "typical" maximum suggesting about 5% maximum transfer efficiency (may be as low as nominally 1%)

Geochemical Modeling of Deep Subsurface Brines Must Factor in the Geothermal Gradient

Temperature of the Earth increases with depth

Increase is nominally about 22° C per Kilometer (or about 3,300 feet)

For a 3 kilometer deep well base temperatures will approach near-boiling conditions

$15° + (3 * 22°) = 81° C$

This temperature increase must be factored into the geochemical behavior of NORM forming constituents

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Applicable Assumptions Allow an Estimate as to the Geochemical Composition of the Brine at Depth

Temperature of 81° C

Equilibrium with respect to:

- Barite [BaSO4]
- Halite [NaCl]
- Dolomite [Ca,Mg(CO3)2]
- Amorphous Silica [SiO_2]
- Near neutral pH
- Use of specialty adapted "ARCADIS Brine Model"

Constituent	Concentration (mg/kg)
Ba+2	42
CO_3-2	23
Ca+2	8
Cl-	228,000
Mg+2	6
Na+	148,000
$SO4^{-2}$	29
SiO_2	87

6 Molar NaCl Brine

$RaSO_4$ 5 orders of magnitude undersaturated - it is in solution

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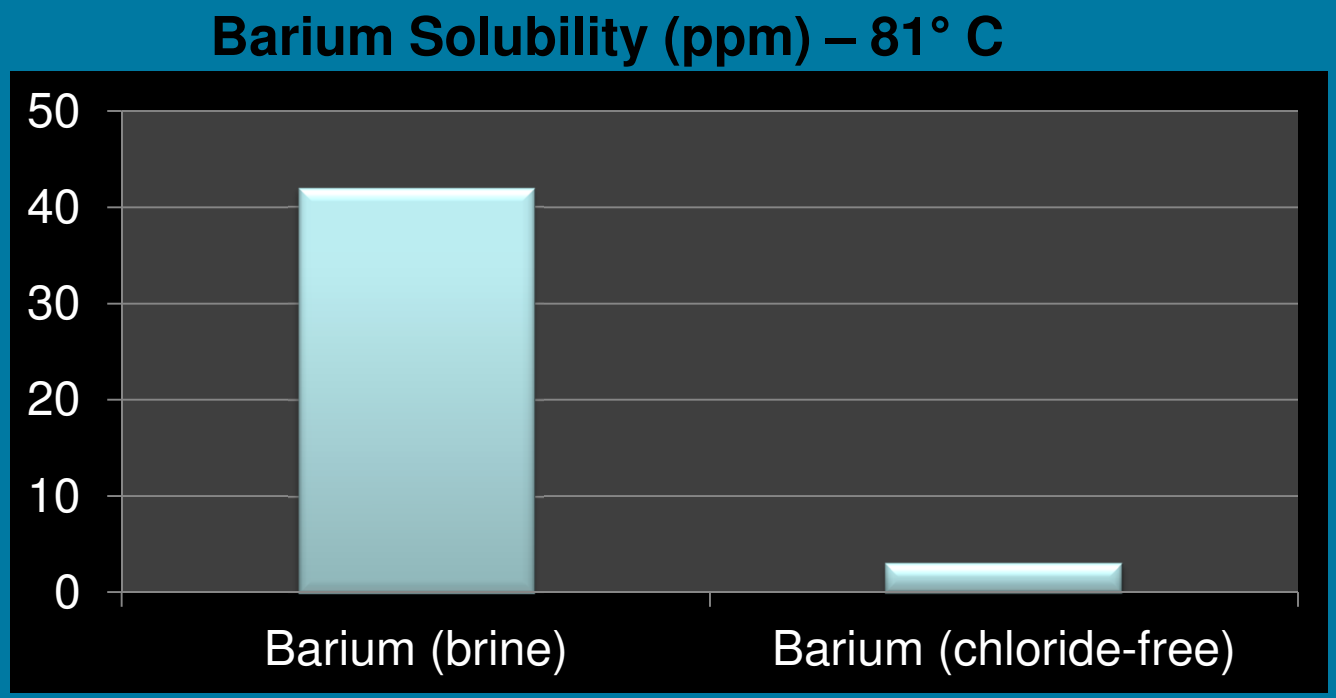
Modeling Results Also Document Relationship Between Barium and Total Dissolved Solids

Empirical relationship has been noted between NORM formation and Total Dissolved Solids (and depth)

Function of barium solubility

Barium solubility can be shown to be a function of chloride concentration (activity)



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Modeling can Assess the Impact of Cooling on the Brine as it is Pumped to the Surface

Constituent	Equilibrium Concentration (mg/kg) – 81° C	Equilibrium Concentration (mg/kg) – 15° C	Precipitated mass (in mg/kg) of brine
Ba^{+2}	42	19	23
$SO4^{-2}$	29	13	16

Barite becomes supersaturated (available for potential precipitation) by a factor of 7 strictly due to cooling

Precipitate 40 milligrams of barite per kilogram of brine (0.17 moles per kilogram of brine) – conservative estimate – no oxidation of sulfides to sulfate

Above model would predict about 133 metric tons per well per year – matches EPA estimate of nominally 100 tons per well per year

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An Estimate as to the Radium Activity within the Barite Scale can Also be Made

- Although remaining undersaturated some radium (up to 38%) will be incorporated into the barite *[Curti, et al, 2010]*
- $4.9 * 10^{-7}$ milligrams of radium will be concentrated within 40 milligrams of barite
- Equates to about 450Bq/g of barite
- Radium-enriched scale is “diluted” though by an equal mass of silica scale formation
- Increased scale mass but at lower activity (250 Bq/g)
- Consistent with “near maximum” radium activities that have been reported

Removal of Sulfate Ion Can Lead to Dissolution of Sulfate Minerals and Release of Radium

Bacterial Reduction of Sulfate Ion Under Reducing Conditions can Modestly Destabilize Barite or Other Sulfate Minerals

$$SO_4^{-2} + 2CH_2O \rightarrow H_2S + HCO_3^-$$

$$Ba(Ra)SO_4 = Ba^{+2} + Ra^{+2} + SO_4^{-2}$$

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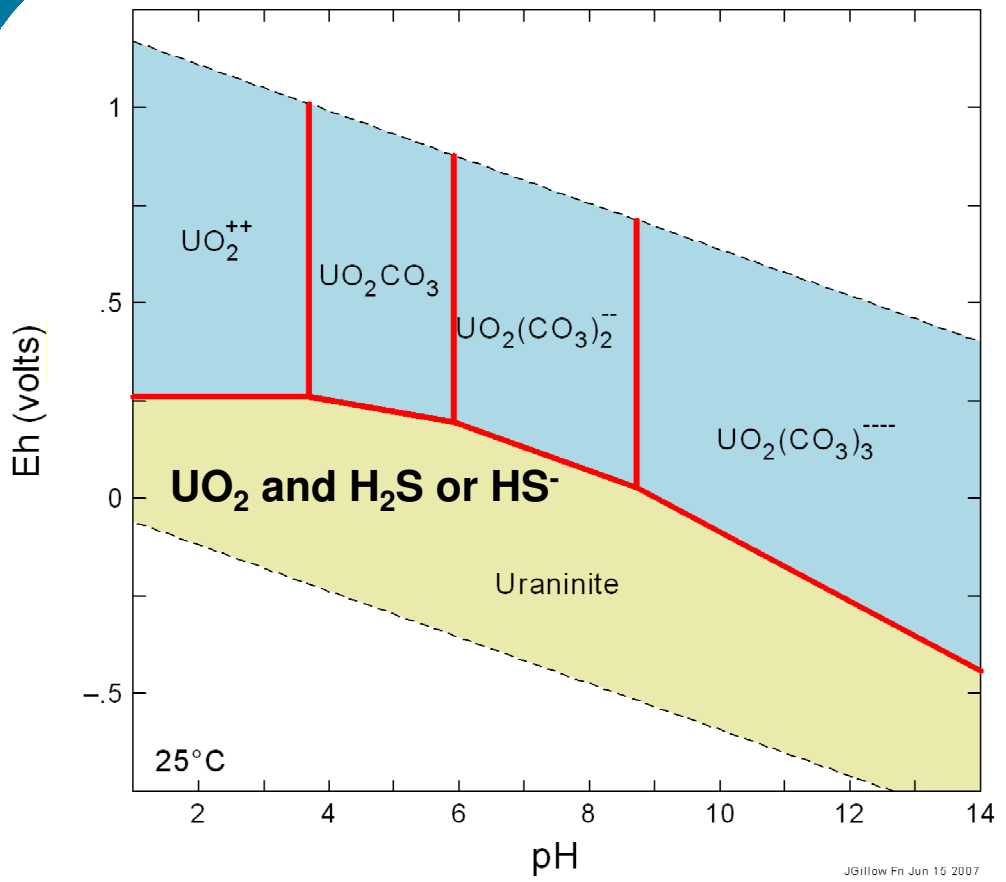
The Geochemical Behavior of Uranium can Help Explain The Potential Separation From Radium

U^{+4} Oxidation state (Uraninite [UO_2]) is stable under low Eh conditions (sulfides)

UO_2^{+2} oxidation state is stable under high Eh conditions (sulfate)

Uranium may be oxidized and transported away from radium which is immobile as a sulfate

Radium may be mobilized in sulfate deficient conditions



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Geochemical Modeling can Identify Locations and Conditions Leading to NORM Formation and Activity

Assess effects of:

- Cooling
- Sulfide oxidation (formation of new sulfate ion)
- Mixing of multiple solutions
- Reactions with surface soils and sediments
- Changing geochemical conditions

Direct benefit in proactively understanding likely areas of NORM and insight into its radioactivity

NORM is Regulated Primarily at the State Level

- NORM is not subject to regulatory control under the Atomic Energy (1954) or Low Level Radioactive Waste Policy Act
- NORM is subject primarily only to individual state radiation control regulations
- Regulations often address radiochemicals associated with medical use or radioactive sources associated with metal analysis instrumentation rather than oil and gas-related NORM
- Various degrees of sophistication as to development and applications of regulations
- NORM-containing wastes that have a specific activity greater than 2,000 pCi/g (70 Bq/g) are subject to the U.S. Department of Transportation (DOT) regulations

Nonetheless EPA Screening Action Levels have been Established for Radium

Based on NUREG-1757 and MOU between EPA and NRC

Radionuclide	Screening Value (pCi/g)	Residential Soil Concentration (pCi/g)	Industrial and Commercial Soil Concentrations (pCi/g)
Radium-226	0.7	5.0	5.0
Radium-226 + C	0.6	No Screen Level Established	No Screen Level Established

Based on estimated 0.25 mSv/y

In addition to background activity of radium

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Disposal Options are Based Radioactivity of the NORM

Non-Mandatory EPA Recommendations
0,1-2 Bq/g
Disposal in sanitary landfills, with limited access and no future development of the site
2-75 Bq/g
Disposal in TENORM or Low-Level Radioactive Waste facilities
Greater than 75 Bq/g
Disposal according to Atomic Energy Act regulations

Typical Action-Based Remedial Alternatives are Often Employed

- Excavation and Off Site Disposal
- On Site Disposal
- In Situ Capping
- Deep Well Injection

Imagine the result