Supporting information for:

**Radium speciation in waste solids from hydraulic fracturing and its removal from wastewater by co-precipitation with barite**

Authors: Bingjie Ouyang,**†** Devon J. Renock,**†** Moses Ajemigbitse,**‡** Katherine Van Sice,**‡** Nathaniel R. Warner,**‡** Joshua D. Landis,**†** Xiaohong Feng**†**

† Department of Earth Sciences, Dartmouth College, HB6105 Fairchild Hall, Hanover, New Hampshire 03755, United States

‡ Department of Civil and Environmental Engineering, The Pennsylvania State University, 212 Sackett Building, University Park, Pennsylvania 16802, United States

*Corresponding author.

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Section 1. Materials characterization

Ra calibration process:
In Ra calibration, we used two Ra sources - a natural U-ore and a NIST-traceable Ra-226 standard. The NIST Ra-226 standard was used as a secondary, independent comparison to confirm data quality.

In our measurements, samples were precipitated using the two Ra sources with theoretically 100 Bq in each sample. The measured Ra-226 in the NIST Ra-226 standard was 99.9 ± 1.2 Bq, and that in the U-ore standard was 100.8 ± 0.7 Bq. The difference between these two sources of Ra-226 was 0.9%, which was calculated as \((\text{NIST}_{Ra} - \text{Uore}_{Ra}) / \text{NIST}_{Ra} \times 100\%\). The agreement between these two sources was then 1 – 0.9% = 99.1% with error of 1.4% (1 sigma), or 2.8% (2 sigma).

Table S1. Characterization of liquid portion of wastewater for acquiring RWS

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (ppm)</td>
<td>40700 ± 200</td>
</tr>
<tr>
<td>Ca (ppm)</td>
<td>14850 ± 90</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>1092 ± 5</td>
</tr>
<tr>
<td>K (ppm)</td>
<td>1130 ± 10</td>
</tr>
<tr>
<td>Ba (ppm)</td>
<td>7220 ± 60</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>4290 ± 40</td>
</tr>
<tr>
<td>S (ppm)</td>
<td>193 ± 3</td>
</tr>
<tr>
<td>Ra-226 in liquid (Bq/L)</td>
<td>288 ± 7</td>
</tr>
<tr>
<td>Ra-226 in RWS (Bq/g)</td>
<td>42.7 ± 0.8</td>
</tr>
</tbody>
</table>

Table S2. Characterization of Flowback and AMD for synthesizing WTS

<table>
<thead>
<tr>
<th>Type</th>
<th>Flowback I</th>
<th>Flowback II</th>
<th>AMD I</th>
<th>AMD II</th>
<th>AMD III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (ppm)</td>
<td>25900 ± 200</td>
<td>39500 ± 200</td>
<td>120 ± 2</td>
<td>1860 ± 20</td>
<td>88 ± 1</td>
</tr>
<tr>
<td>Ca (ppm)</td>
<td>8240 ± 50</td>
<td>15400 ± 90</td>
<td>163 ± 2</td>
<td>264 ± 3</td>
<td>99 ± 1</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>759 ± 4</td>
<td>1608 ± 7</td>
<td>47 ± 1</td>
<td>107 ± 1</td>
<td>23 ± 1</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>210 ± 3</td>
<td>68 ± 2</td>
<td>61 ± 2</td>
<td>1 ± 0.01</td>
<td>14 ± 0.1</td>
</tr>
<tr>
<td>Ba (ppm)</td>
<td>4590 ± 40</td>
<td>728 ± 7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>1980 ± 20</td>
<td>3320 ± 30</td>
<td>1 ± 0.01</td>
<td>6 ± 0.03</td>
<td>1 ± 0.01</td>
</tr>
<tr>
<td>Cl (ppm)</td>
<td>60400 ± 400</td>
<td>103100 ± 900</td>
<td>73 ± 2</td>
<td>840 ± 10</td>
<td>64 ± 1</td>
</tr>
<tr>
<td>Br (ppm)</td>
<td>576 ± 8</td>
<td>1060 ± 10</td>
<td>-</td>
<td>5 ± 0.02</td>
<td>-</td>
</tr>
<tr>
<td>SO₄ (ppm)</td>
<td>20 ± 0.2</td>
<td>-</td>
<td>615 ± 9</td>
<td>3800 ± 30</td>
<td>589 ± 8</td>
</tr>
<tr>
<td>Ra-226 (Bq/L)</td>
<td>370 ± 10</td>
<td>360 ± 10</td>
<td>6 ± 0.2</td>
<td>54 ± 2</td>
<td>54 ± 2</td>
</tr>
</tbody>
</table>

- : measurements below detection limit.
Figure S1. Mineralogical composition of RWS by XRD analysis (*Corundum was added as an internal standard)

Figure S2. Mineralogical composition of WTS's by XRD analysis
Section 2. Elemental recovery

Both RWT and WTS are digested completely without transfer between steps, termed as bulk digestion, in order to compare and make sure that the SE procedure has recovered over 80% of the total elemental composition. In bulk digestion, 250 mg aliquot of solid sample was added to teflon vials for reaction following a sequence of steps: (1) Add 2 mL concentrated HNO$_3$ and warm up to 80 °C; (2) At 80 °C, continuously add hydrogen peroxide until the bubbling of liquid almost stops to completely decompose organic matter; (3) After evaporating the solution in step (2) to dryness, add 10 mL reverse aqua regia (HNO$_3$ : HCl : HF = 1:3:1) and heat up the solution to 95 °C for 2 h, then evaporate the solution to dryness; (4) Repeat step (3) until no visible particles remain in 6 mL 4 M HCl solution. Note if one solid sample cannot be completely digested following the above steps, the residual needs to be digested by other methods.
Figure S4. Comparison of elemental recovery by SE and bulk digestion.

Figure S5. Na, Ca, Fe, and S extracted during SE of WTS's.

Section 3. PHREEQC program input

PHREEQC is a computer program developed by the USGS and used to perform a variety of low-temperature aqueous, geochemical reactions. The inputs for calculating liquid mixtures of WTS are given below:

```
TITLE WTS 1. --Calculate activities of ions.
SOLUTION 1  Titration experiment11
    units  ppm
    temp  25.0
    Na    2714.74
    Ca    976.98
    Mg    118.72
    Fe    76.01
    Ba    462.34
    Sr    200.34
    Cl    6145.26
    Br    58.02
    S(6)  555.07
    Ra    0.00000115
SOLUTION_MASTER_SPECIES
    Ra     Ra+2  0.0    226.0250  226.0250
```
Ra(2)   Ra+2    0.0     226.0250  
SOLUTION_SPECIES
#primary master species for Ra
#secondary master species for Ra+2
Ra+2 = Ra+2
    log_k          0.0
Ra+2 + OH− = RaOH+
    log_k          0.5
delta_h        1.1 kcal
Ra+2 + SO4−2 = RaSO4
    log_k          2.75
delta_h        1.3 kcal
Ra+2 + Cl− = RaCl+
    log_k         -0.1
delta_h        0.5 kcal

PHASES
Barite
BaSO4 = Ba+2 + SO4−2
    log_k          -9.97
delta_h        6.35 kcal
Celestite
SrSO4 = Sr+2 + SO4−2
    log_k          -6.63
delta_h        -4.037 kcal
RadiumSulfate
RaSO4 = Ra+2 + SO4−2
    log_k          -10.26
delta_h        38.74 kcal

END

TITLE WTS 2.--Calculate activities of ions.
SOLUTION 1 Titration experiment
units    ppm
  temp    ppm
Na      11355.14
Ca      3418.51
Mg      364.74
Fe      83.62
Ba      1814.43
Sr      786.33
Cl      24367.77
Br      230.72
S(6)    2306.36
Ra      0.00000482
SOLUTION_MASTER_SPECIES
  Ra      Ra+2    0.0     226.0250  226.0250
  Ra(2)   Ra+2    0.0     226.0250
SOLUTION_SPECIES
#primary master species for Ra
#secondary master species for Ra+2
Ra+2 = Ra+2
    log_k          0.0
Ra+2 + OH− = RaOH+
    log_k          0.5
delta_h        1.1 kcal
Ra\(^{2+} + SO_4^{-2} = RaSO_4\)
\[
\begin{align*}
\text{log}_k &= 2.75 \\
\text{delta}_h &= 1.3 \text{ kcal}
\end{align*}
\]
Ra\(^{2+} + Cl^- = RaCl^+\)
\[
\begin{align*}
\text{log}_k &= -0.1 \\
\text{delta}_h &= 0.5 \text{ kcal}
\end{align*}
\]

**PHASES**

**Barite**
BaSO\(_4 = Ba^{2+} + SO_4^{-2}\)
\[
\begin{align*}
\text{log}_k &= -9.97 \\
\text{delta}_h &= 6.35 \text{ kcal}
\end{align*}
\]

**Celestite**
SrSO\(_4 = Sr^{2+} + SO_4^{-2}\)
\[
\begin{align*}
\text{log}_k &= -6.63 \\
\text{delta}_h &= -4.037 \text{ kcal}
\end{align*}
\]

**RadiumSulfate**
RaSO\(_4 = Ra^{2+} + SO_4^{-2}\)
\[
\begin{align*}
\text{log}_k &= -10.26 \\
\text{delta}_h &= 38.74 \text{ kcal}
\end{align*}
\]

---

**TITLE** WTS 3.--Calculate activities of ions.

**SOLUTION 1** Titration experiment11

**SOLUTION_MASTER_SPECIES**

```
<table>
<thead>
<tr>
<th>Species</th>
<th>Master Species</th>
<th>Amount</th>
<th>Activity 1</th>
<th>Activity 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra</td>
<td>Ra(^{2+})</td>
<td>0.0</td>
<td>226.0250</td>
<td>226.0250</td>
</tr>
<tr>
<td>Ra(2)</td>
<td>Ra(^{2+})</td>
<td>0.0</td>
<td>226.0250</td>
<td></td>
</tr>
</tbody>
</table>

**SOLUTION_SPECIES**

```

---

**PHASES**

**Barite**
BaSO\(_4 = Ba^{2+} + SO_4^{-2}\)
\[
\begin{align*}
\text{log}_k &= -9.97
\end{align*}
\]
delta_h 6.35 kcal

Celestite
SrSO₄ = Sr⁺² + SO₄⁻²
log_k -6.63
delta_h -4.037 kcal

RadiumSulfate
RaSO₄ = Ra⁺² + SO₄⁻²
log_k -10.26
delta_h 38.74 kcal

---

TITLE WTS 4.--Calculate activities of ions.
SOLUTION 1  Titration experiment

units ppm
temp 25.0
Na 8984.15
Ca 3128.80
Mg 391.10
Fe 13.68
Ba 137.79
Sr 633.24
Cl 20188.25
Br 204.11
S(6) 3081.58
Ra 0.00000300

SOLUTION_MASTER_SPECIES
Ra Ra⁺² 0.0 226.0250 226.0250
Ra(2) Ra⁺² 0.0 226.0250

SOLUTION_SPECIES
#primary master species for Ra
#secondary master species for Ra⁺²
Ra⁺² = Ra⁺²
log_k 0.0
Ra⁺² + OH⁻ = RaOH⁺
log_k 0.5
delta_h 1.1 kcal
Ra⁺² + SO₄⁻² = RaSO₄
log_k 2.75
delta_h 1.3 kcal
Ra⁺² + Cl⁻ = RaCl⁺
log_k -0.1
delta_h 0.5 kcal

PHASES
Barite
BaSO₄ = Ba⁺² + SO₄⁻²
log_k -9.97
delta_h 6.35 kcal

Celestite
SrSO₄ = Sr⁺² + SO₄⁻²
log_k -6.63
delta_h -4.037 kcal

RadiumSulfate
RaSO₄ = Ra⁺² + SO₄⁻²
log_k -10.26
delta_h 38.74 kcal

END
TITLE WTS 5.--Calculate activities of ions.  
SOLUTION 1  Titration experiment11  
units  ppm  
temp  25.0  
Na  20037.83  
Ca  7844.16  
Mg  825.31  
Fe  41.33  
Ba  368.50  
Sr  1681.03  
Cl  52199.71  
Br  535.04  
S(6)  290.86  
Ra  0.00000559  
SOLUTION_MASTER_SPECIES  
Ra  Ra+2  0.0  226.0250  226.0250  
Ra(2)  Ra+2  0.0  226.0250  
SOLUTION_SPECIES  
#primary master species for Ra  
#secondary master species for Ra+2  
Ra+2 = Ra+2  
log_k  0.0  
Ra+2 + OH- = RaOH+  
log_k  0.5  
delta_h  1.1 kcal  
Ra+2 + SO4-2 = RaSO4  
log_k  2.75  
delta_h  1.3 kcal  
Ra+2 + Cl- = RaCl+  
log_k  -0.1  
delta_h  0.5 kcal  
PHASES  
Barite  
BaSO4 = Ba+2 + SO4-2  
log_k  -9.97  
delta_h  6.35 kcal  
Celestite  
SrSO4 = Sr+2 + SO4-2  
log_k  -6.63  
delta_h  -4.037 kcal  
RadiumSulfate  
RaSO4 = Ra+2 + SO4-2  
log_k  -10.26  
delta_h  38.74 kcal  
END  

TITLE WTS 6.--Calculate activities of ions.  
SOLUTION 1  
units  ppm  
temp  25.0  
Na  22095.70  
Ca  8665.89  
Mg  918.10  
Fe  64.91
Ba              406.25
Sr              1853.14
Cl              57544.65
Br              589.85
S(6)            271.80
Ra              0.00000544

SOLUTION_MASTER_SPECIES
Ra      Ra+2    0.0     226.0250     226.0250
Ra(2)   Ra+2    0.0     226.0250

SOLUTION_SPECIES
#primary master species for Ra
#secondary master species for Ra+2
Ra+2 = Ra+2
  log_k          0.0
Ra+2 + OH- = RaOH+
  log_k          0.5
  delta_h        1.1 kcal
Ra+2 + SO4-2 = RaSO4
  log_k          2.75
  delta_h        1.3 kcal
Ra+2 + Cl- = RaCl+
  log_k          -0.1
  delta_h        0.5 kcal

PHASES
Barite
BaSO4 = Ba+2 + SO4-2
  log_k          -9.97
  delta_h        6.35 kcal
Celestite
SrSO4 = Sr+2 + SO4-2
  log_k          -6.63
  delta_h        -4.037 kcal
RadiumSulfate
RaSO4 = Ra+2 + SO4-2
  log_k          -10.26
  delta_h        38.74 kcal
END