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,[†] Xiahong 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 $(NIST_{Ra} - Uore_{Ra})/NIST_{Ra} \times 100\%$. 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

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

Table S2. Characterization of Flowback and AMD for synthesizing WTS

Type	Flowback I	Flowback II	AMD I	AMD II	AMD III
Na (ppm)	25900 ± 200	39500 ± 200	120 ± 2	1860 ± 20	88 ± 1
Ca (ppm)	8240 ± 50	15400 ± 90	163 ± 2	264 ± 3	99 ± 1
Mg (ppm)	759 ± 4	1608 ± 7	47 ± 1	107 ± 1	23 ± 1
Fe (ppm)	210 ± 3	68 ± 2	61 ± 2	1 ± 0.01	14 ± 0.1
Ba (ppm)	4590 ± 40	728 ± 7	-	-	-
Sr (ppm)	1980 ± 20	3320 ± 30	1 ± 0.01	6 ± 0.03	1 ± 0.01
Cl (ppm)	60400 ± 400	103100 ± 900	73 ± 2	840 ± 10	64 ± 1
Br (ppm)	576 ± 8	1060 ± 10	-	5 ± 0.02	-
SO_4 (ppm)	20 ± 0.2	-	615 ± 9	3800 ± 30	589 ± 8
Ra-226 (Bq/L)	370 ± 10	360 ± 10	6 ± 0.2	54 ± 2	54 ± 2

- : measurements below detection limit.

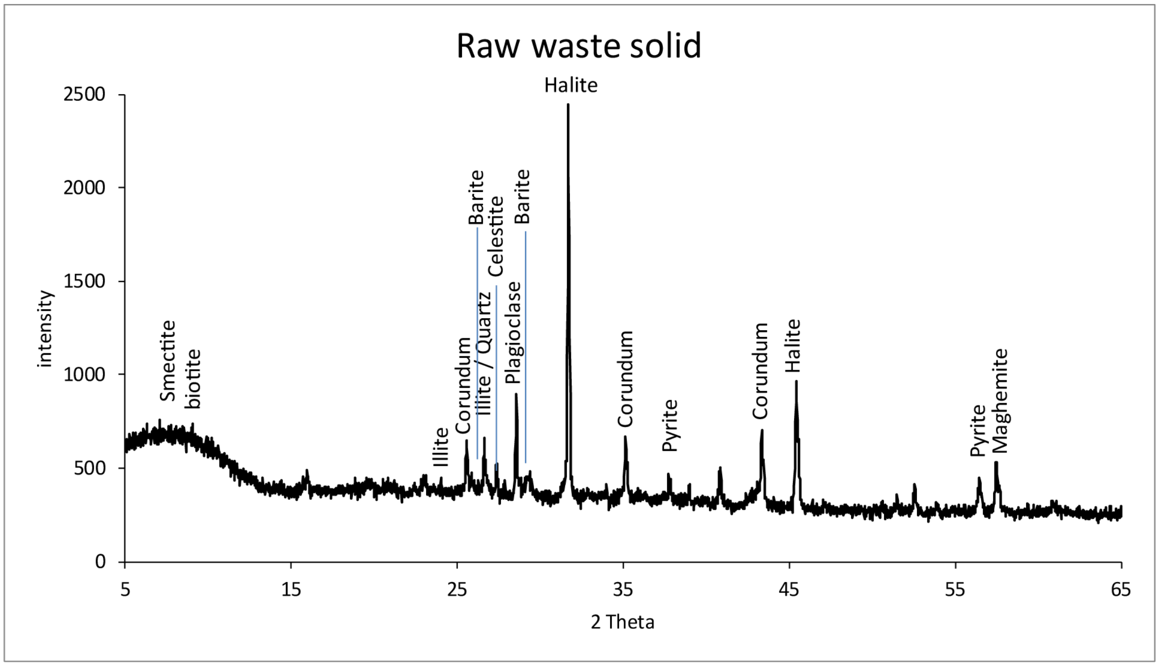

Figure S1. Mineralogical composition of RWS by XRD analysis (* Corundum was added as an internal standard)

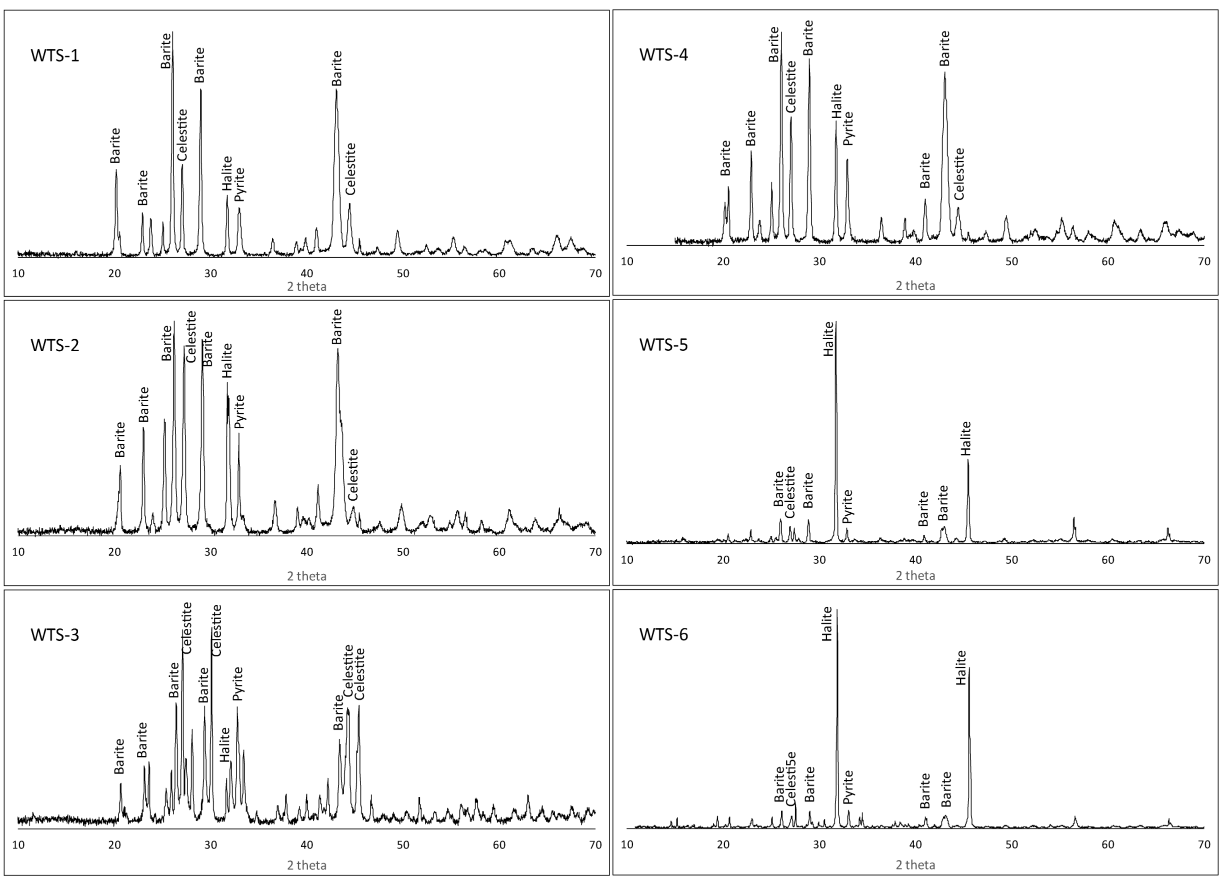

Figure S2. Mineralogical composition of WTS's by XRD analysis

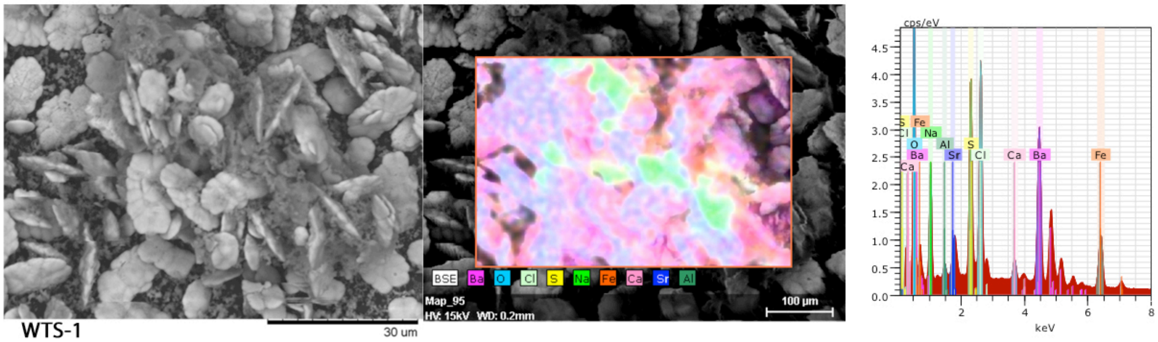

Figure S3. SEM-EDS analysis indicate the unreacted WTS solids may contain amorphous iron oxides

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.

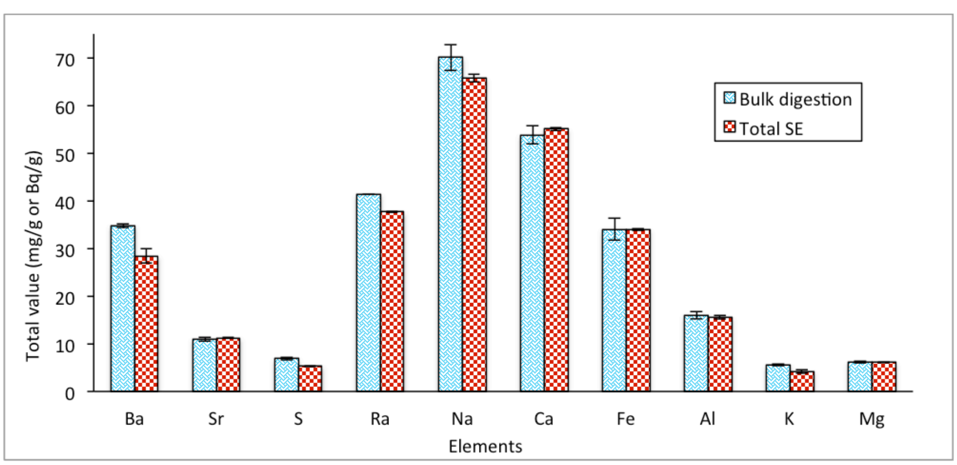

Figure S4. Comparison of elemental recovery by SE and bulk digestion.

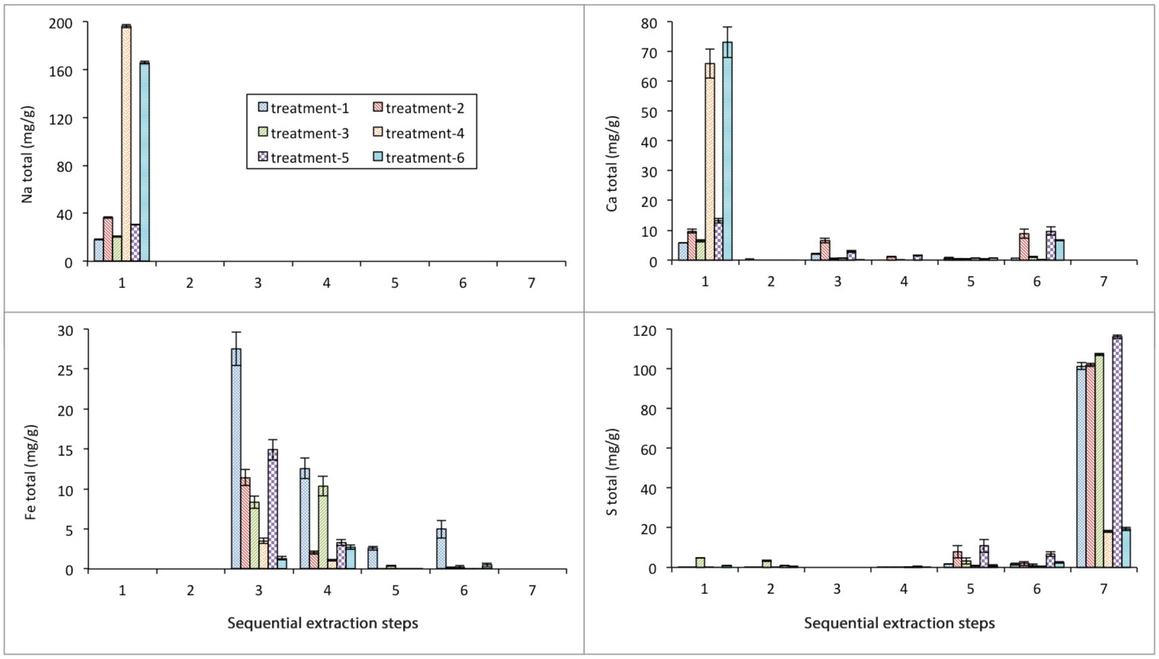

Figure S5. Na, Ca, Fe, and S extracted during SE of WTS's.

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 experiment11
        units   ppm
        temp    25.0
        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 + 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 3.--Calculate activities of ions.
SOLUTION 1  Titration experiment11
        units   ppm
        temp    25.0
        Na              2368.33
        Ca              819.12
        Mg              88.07
        Fe              31.33
        Ba              405.81
        Sr              175.97
        Cl              5394.65
        Br              50.93
        S(6)            538.69
        Ra              0.00000221
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 4.--Calculate activities of ions.
SOLUTION 1  Titration experiment11
        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
```