Supplementary Materials: Optimisation of Radium Removal from Saline Produced Waters during Oil and Gas Extraction

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Table S1. Characterisation of production water from hydraulic fracturing operations.

Location	Na^+	Ca^{2+}	Ba^{2+}	Cl^-	SO_4^{2-}	TDS	^{226}Ra	pH
	mg/dm³						Bq/dm³	
	Range							
Bowland Shale, West Lancashire, UK [1]	<200–33,300	nr	nr	15,400– 92,800	nr	nr	14–90	6–8
Lower Saxony, Germany [2]	3200–44,800	612–22,000	≤455	7010–115,140	4–1100	nr	nr	nr
Marcellus Shale, Pennsylvania, USA [3–6]	8–82,000	16–40,000	0.06–22,400	18–200,000	1–1700	2.8–390,000	0.002–629	5.8–6.6
DJ Basin, Colorado, USA [7]	nr	nr	nr	13,600	1.3	22,500	nr	6.8
West Texas Region, USA [8]	540–74,600	137–20,100	≤2175	1200–153,000	≤2000	2900–252,000	nr	nr

nr—not reported, TDS—total dissolved solids.

Table S2. ^{226}Ra recovery by co-precipitation at 0.3 and 3 M NaCl (all 0.22 mM Ba).

SO_4^{2-} (mM)	^{226}Ra Recovery	
	% ± 2σ*	Mean %
Low salinity (0.3 M)		
0.11	21.9 ± 5.9	12.0
	9.5 ± 2.3	
	4.6 ± 1.1	
0.18	20.9 ± 5.6	21.2
	25.1 ± 7.4	
	17.6 ± 4.7	
0.35	70.8 ± 22.3	64.5

	66.0 ± 21.9	
	56.8 ± 17.3	
0.75	68.3 ± 22.4 72.7 ± 21.6 74.9 ± 21.9	72.0
1.46	92.5 ± 27.0 103.7 ± 26.7 78.0 ± 22.5	91.4
2.54	107.8 ± 27.7 92.4 ± 24.9 86.6 ± 22.7	95.6
3.58	84.3 ± 24.9 73.0 ± 24.1 111.7 ± 27.8	89.6
	High salinity (3 M)	
0.10	5.9 ± 1.6 8.1 ± 2.6 3.1 ± 0.9	5.7
0.15	11.6 ± 3.7 6.2 ± 2.0 9.2 ± 2.5	9.0
0.34	13.1 ± 3.6 10.8 ± 3.6 10.6 ± 3.1	11.5
1.49	23.4 ± 8.2 21.2 ± 7.3 18.3 ± 6.1	21.0
3.48	48.1 ± 22.3 42.3 ± 24.6 41.6 ± 21.4	44.0

7.15	70.7 ± 22.9 68.1 ± 19.9 71.3 ± 26.5	70.0
14.69	111.6 ± 31.3 93.3 ± 26.9 90.2 ± 28.0	98.4
35.46	70.6 ± 26.0 87.6 ± 28.7 95.0 ± 29.0	84.4
70.83	89.9 ± 29.8 103.2 ± 27.9 96.8 ± 30.2	96.6

*2σ error based on counting statistics only.

Table 3. ^{226}Ra recovery by co-precipitation at 0.3 and 3 M NaCl (all 5 mM Ba).

SO_4^{2-} (mM)	% ^{226}Ra Recovery ± 2σ*
Low salinity (0.3 M)	
0.50	24.4 ± 4.9
1.25	38.5 ± 9.4
5.00	94.6 ± 18.8
High salinity (3 M)	
0.50	22.5 ± 4.4
1.25	43.6 ± 10.0
5.00	99.6 ± 20.7

*2σ error based on counting statistics only.

Table 4. ^{226}Ra recovery by post-precipitation at 0.3 and 3 M NaCl (all 0.22 mM Ba).

Sampling Interval	% ^{226}Ra Recovery ± 2σ*	
	Low Salinity (0.3 M), 1.5 mM SO_4^{2-}†	High Salinity (3 M), 15 mM SO_4^{2-}†
30 min	26.3 ± 0.2	5.1 ± 0.03
1 h	39.0 ± 0.3	6.2 ± 0.04
2 h	40.7 ± 0.3	13.1 ± 0.1
3 h	59.4 ± 0.6	16.6 ± 0.1
6 h	60.4 ± 0.6	30.3 ± 0.2
24 h	79.9 ± 1.1	63.4 ± 0.6
48 h	84.4 ± 1.3	68.9 ± 0.8
3 d	86.0 ± 1.4	72.7 ± 0.8
4 d	86.7 ± 1.4	74.0 ± 0.9
7 d	87.3 ± 1.5	76.3 ± 1.0
14 d	86.1 ± 1.4	80.1 ± 1.1

*2σ error based on counting statistics only. †Amount of SO_4^{2-} used to precipitate barite before addition of ^{226}Ra.

Table 5. PHREEQC* output for ^{226}Ra recovery by co-precipitation at 0.3 and 3 M NaCl (all 0.22 mM Ba).

Initial SO_4^{2-} Conc. (mM)	NaCl (M)	Ion Activity (mM)		Barite SI	Theoretical % ^{226}Ra Recovery ($a_0 = 1$)	^{226}Ra x_i for $Ba_{1-x}Ra_xSO_4$ ($a_0 = 1$)
		Ba^{2+}	SO_4^{2-}			
Low salinity (0.3 M)						
0.11	0.29	0.06	0.02	1.11	35.3	4.15×10^{-8}
0.18	0.29	0.06	0.04	1.33	60.3	4.67×10^{-8}
0.35	0.29	0.06	0.08	1.63	92.1	5.33×10^{-8}
0.75	0.29	0.06	0.17	1.96	97.8	5.45×10^{-8}
1.46	0.29	0.06	0.34	2.23	99.0	5.48×10^{-8}
2.54	0.29	0.05	0.58	2.46	99.5	5.49×10^{-8}
3.58	0.29	0.05	0.82	2.59	99.6	5.49×10^{-8}
High salinity (3 M)						
0.10	3.02	0.04	0.01	0.26	4.8	1.64×10^{-8}
0.15	3.02	0.04	0.01	0.44	11.1	1.90×10^{-8}
0.34	3.02	0.04	0.02	0.79	38.5	3.01×10^{-8}
1.49	3.02	0.04	0.08	1.42	85.2	4.90×10^{-8}
3.48	3.03	0.04	0.18	1.79	93.8	5.25×10^{-8}
7.15	3.04	0.04	0.38	2.09	97.0	5.38×10^{-8}
14.69	3.07	0.04	0.77	2.39	98.5	5.44×10^{-8}
35.46	3.15	0.04	1.82	2.73	99.3	5.47×10^{-8}
70.83	3.28	0.03	3.52	2.97	99.6	5.49×10^{-8}

*SIT database; x_i—mole fraction; a_0—non-dimensional Guggenheim parameter.

Table 6. PHREEQC* output for ^{226}Ra recovery by co-precipitation at 0.3 and 3 M NaCl (all 5 mM Ba).

Initial SO_4^{2-} conc. (mM)	NaCl (M)	Ion Activity (mM)		Barite SI	Theoretical % ^{226}Ra Recovery ($a_0 = 1$)	^{226}Ra x_i for $Ba_{1-x}Ra_xSO_4$ ($a_0 = 1$)
		Ba^{2+}	SO_4^{2-}			
Low salinity (0.3 M)						
0.50	0.301	1.28	0.10	3.07	6.6	1.61×10^{-9}
1.25	0.303	1.26	0.25	3.46	17.6	1.70×10^{-9}
5.00	0.312	1.14	1.00	4.02	98.7	2.41×10^{-9}
High salinity (3 M)						
0.50	3.037	0.99	0.03	2.30	2.8	6.85×10^{-9}
1.25	3.040	0.99	0.07	2.70	8.0	7.77×10^{-9}
5.00	3.053	0.98	0.26	3.29	92.0	2.28×10^{-9}

*SIT database; x_i—mole fraction; a_0—non-dimensional Guggenheim parameter.

References

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