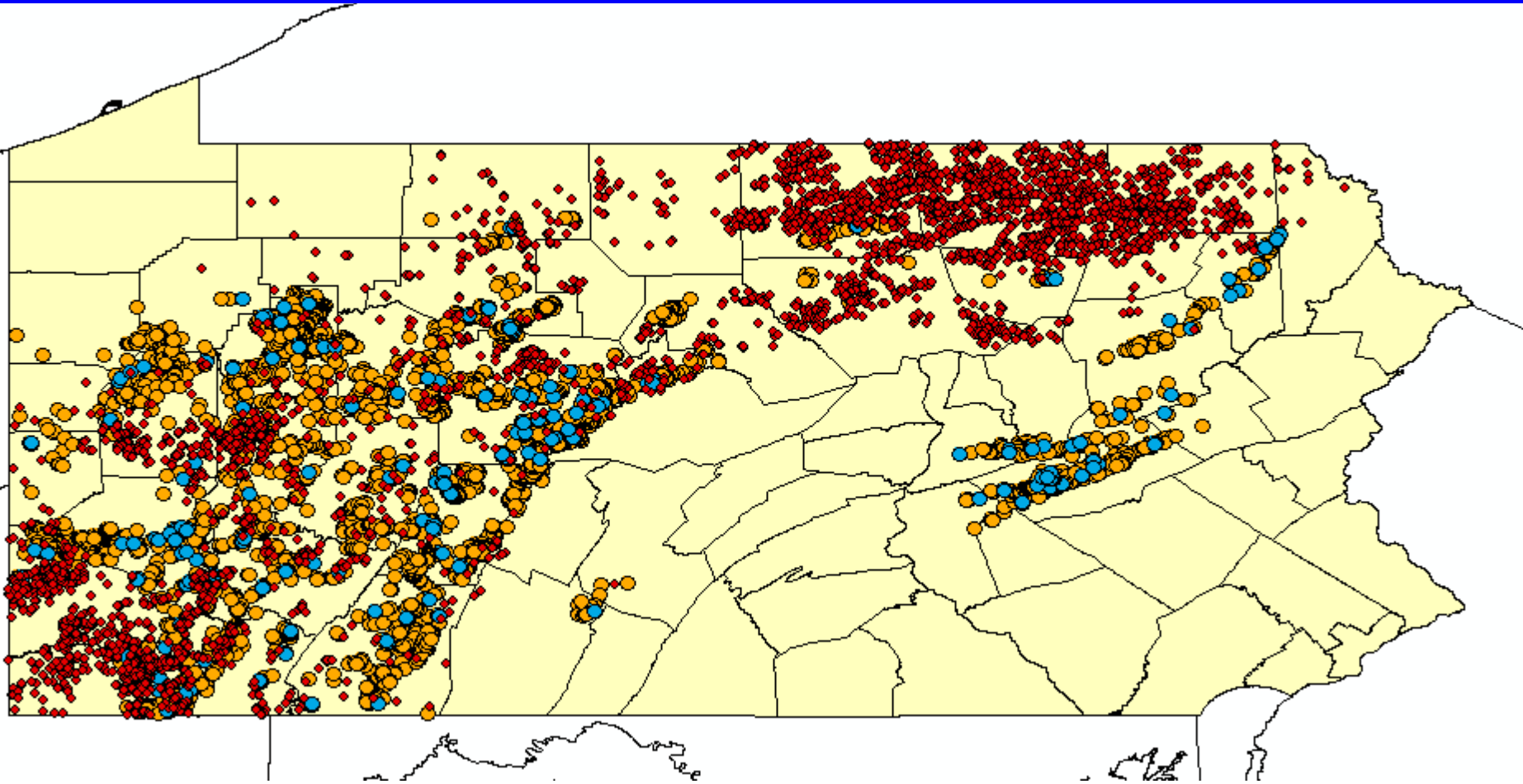# Application of AMD for produced water reuse can facilitate byproduct recovery and permanent NORM sequestration

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# Why AMD?



◆ Well permits     ● Abandoned discharge     ● Reclaimed discharge

# Technical aspects of AMD use

**Water source**

   - Fresh water (withdrawal costs)

   - Treated AMD = $0.09 – 0.76 /1000 gal

   - Municipal water = $8 – 14.5 /1000 gal

**Transport**

   - Same for any water source

   - Trucks cost $1 /bbl/hr

**Storage**

   - Impoundment (single or double liner)

   - Centralized tank farms

**AMD can be economical if used locally**

# AMD selection criteria

**Accessibility**

     - Proximity to wells

**Quantity**

     - Sufficient flowrate to support hydraulic fracturing needs in the area

     - Reliable source, no depletion during the summer
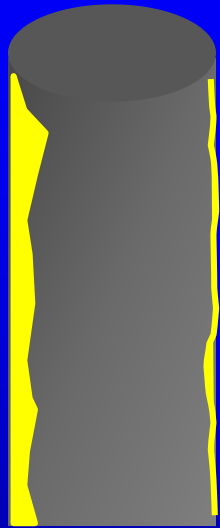
**Quality**

     - Circumneutral pH

     - Iron

     - Sulfate

Wide range of industry standards. AMD use will depend on water source, well site and industry preference/tolerance.
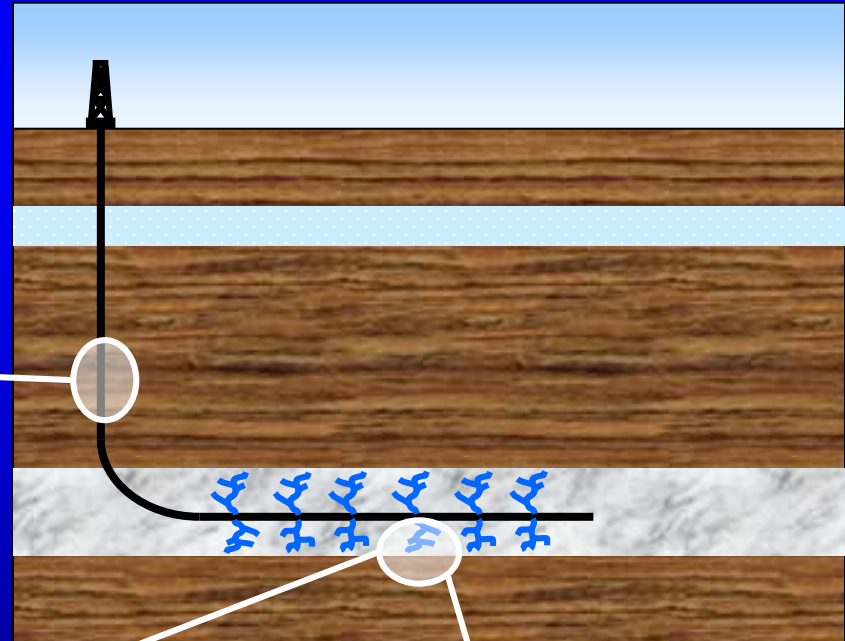
# Sulfate precipitation downhole

Microbial sulfate reduction NOT POSSIBLE in Marcellus

Scaling in production casing

"Homogeneous " scaling

Formation of plugs

# Sulfate precipitation downhole

Calculations performed using:

- Fracturing fluid volume = 3 million gal
- $9\%_w$ proppant
- Proppant density = 1201 kg/m$^3$

| $SO_4$ (mg/L) | $BaSO_4$ volume (m$^3$) | Volume percentage compared with proppant |
|---|---|---|
| 200 | 0.98 | 0.1% |
| 800 | 4.9 | 0.5% |
| 2000 | 9.8 | 1.3% |

**Negligible volume compared with the volume of proppant injected**

# Co-treatment of flowback water and AMD



Flowback water

Abandoned mine drainage (AMD)

Barium, Strontium, Calcium

Sulfate

Hydraulic fracturing

**Enables the reuse of flowback water for hydraulic fracturing with limited treatment => decreases the treatment and transport cost of flowback water**

# AMD and flowback water chemistry

## AMD

| | Site A | Site B | Site C | Site D |
|---|---|---|---|---|
| pH | 5.7 | 7.03 | 6.14 | 7.56 |
| Alkalinity (mg/L as $CaCO_3$) | 62 | 394 | 40.5 | 47.5 |
| $SO_4$ | 696 | 242.5 | 709 | 328 |
| Fe | 27 | 0 | 32.1 | 0 |
| TDS | - | 1574 | 1328 | 1127 |

## Flowback

| | FB 1 | FB 2 |
|---|---|---|
| Cl | 104,300 | 29,000 |
| Na | 38,370 | 11,860 |
| Ca | 15,021 | 2,224 |
| Mg | 1,720 | 249 |
| Sr | 1,800 | 367 |
| Ba | 236 | 781 |

Mixing ratio based on flowback water recovery

FB 1 15% + AMD A or B 85%

FB 2 10% + AMD C or D 90%

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# Barium removal



Initial BaSO$_4$ supersaturation

- 10 ⎱ Flowback 1 + AMD B Low sulfate
- 18 ⎰ AMD A High sulfate
- 35 ⎱ Flowback 2 + AMD D Low sulfate
- 52 ⎰ AMD C High sulfate
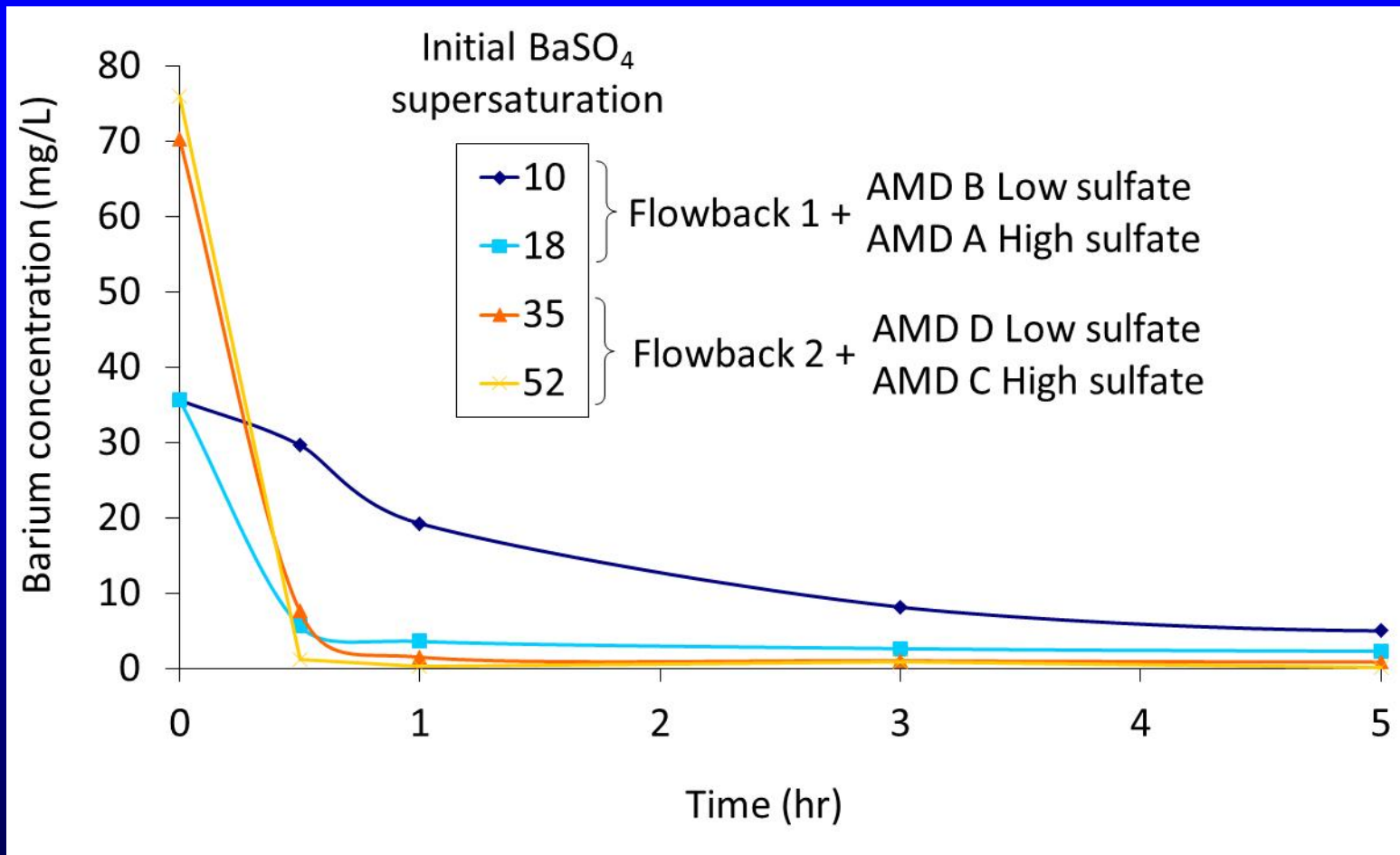
**Fast and total barium removal for supersaturation above 30**

**Residual [SO$_4$] > 200 mg/L in all cases**

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# Adjusting the Mixing Ratio to Achieve Desired Effluent Sulfate Limit

| Flowback Water | AMD | Mixture Components | | Initial Concentration (mg/L) | | Final Sulfate Conc. (mg/L) | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | Flowback Water (%) | AMD (%) | Sulfate | Ba | Measured | Predicted |
| 1 | A | 20 | 80 | 560 | 47 | 530 | 534 |
| | | 70 | 30 | 219 | 165 | 128 | 120 |
| 1 | B | 30 | 70 | 174 | 71 | 140 | 129 |
| | | 40 | 60 | 151 | 94 | 102 | 92 |
| 2 | C | 35 | 65 | 467 | 434 | 155 | 145 |
| | | 40 | 60 | 433 | 496 | 85 | 84 |
| 2 | D | 20 | 80 | 251 | 233 | 120 | 88 |
| | | 25 | 75 | 236 | 291 | 63 | 34 |

Optimum coagulant dose: 20 mg/L
Optimum pH: 6.0
Flocculation time: 30 min
Settling time: 30 min



Flowback 1　　　AMD A　　　Treated Effluent
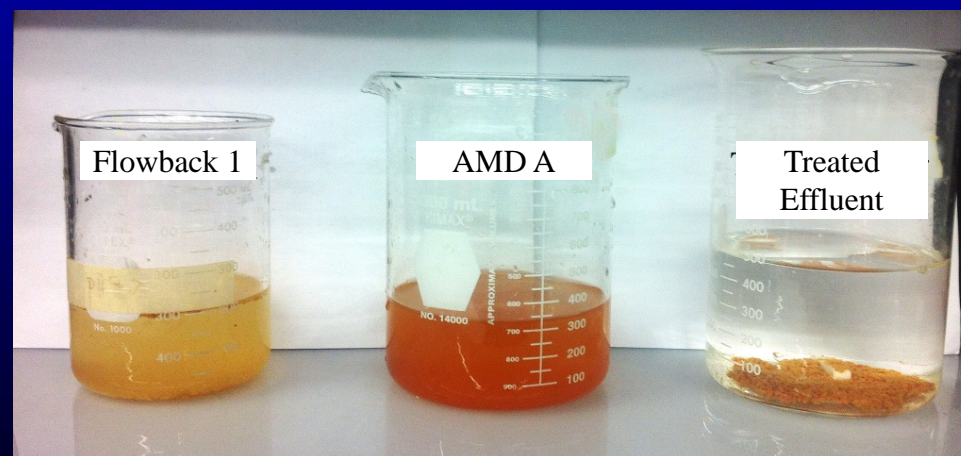
# Radium in flowback water

- Ra-226 activity in produced water is distinctly higher in Marcellus than in other Appalachian Basin formations;

- Ra-226 is directly related with TDS in both flowback and produced waters;
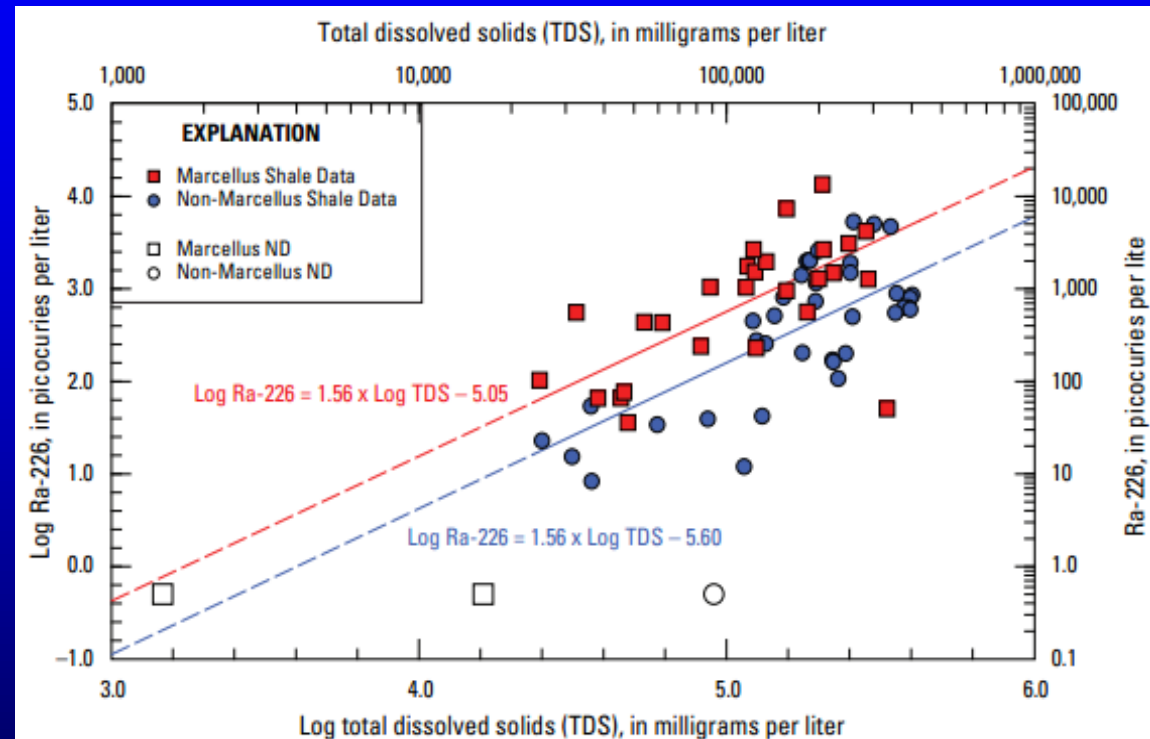


Activity of Ra226 in relation to log total dissolved solids for Marcellus Shale (Red) and non-Marcellus Shale (Blue) data.

Rowan, USGS, 2011.

# Ra removal during sulfate precipitation

**Co-precipitation of Radium with Barium and Strontium Sulfate and Its Impact on the Fate of Radium during Treatment of Produced Water from Unconventional Gas Extraction**

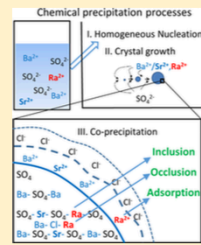Tieyuan Zhang,[†,‡] Kelvin Gregory,[§,‡] Richard W. Hammack,[‡] and Radisav D. Vidic*[,†,‡]

[†]Department of Civil and Environmental Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States
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Ⓢ Supporting Information

ABSTRACT: Radium occurs in flowback and produced waters from hydraulic fracturing for unconventional gas extraction along with high concentrations of barium and strontium and elevated salinity. Radium is often removed from this wastewater by co-precipitation with barium or other alkaline earth metals. The distribution equation for Ra in the precipitate is derived from the equilibrium of the lattice replacement reaction (inclusion) between the $Ra^{2+}$ ion and the carrier ions (e.g., $Ba^{2+}$ and $Sr^{2+}$) in aqueous and solid phases and is often applied to describe the fate of radium in these systems. Although the theoretical distribution coefficient for Ra–$SrSO_4$ ($K_d$ = 237) is much larger than that for Ra–$BaSO_4$ ($K_d$ = 1.54), previous studies have focused on Ra–$BaSO_4$ equilibrium. This study evaluates the equilibria and kinetics of co-precipitation reactions in Ra–Ba–$SO_4$ and Ra–Sr–$SO_4$ binary systems and the Ra–Ba–Sr–$SO_4$ ternary system under varying ionic strength (IS) conditions that are representative of brines generated during unconventional gas extraction. Results show that radium removal generally follows the theoretical distribution law in binary systems and is enhanced in the Ra–Ba–$SO_4$ system and restrained in the Ra–Sr–$SO_4$ system by high IS. However, the experimental distribution coefficient ($K_d$') varies widely and cannot be accurately described by the distribution equation, which depends on IS, kinetics of carrier precipitation and does not account for radium removal by adsorption. Radium removal in the ternary system is controlled by the co-precipitation of Ra–Ba–$SO_4$, which is attributed to the rapid $BaSO_4$ nucleation rate and closer ionic radii of $Ra^{2+}$ with $Ba^{2+}$ than with $Sr^{2+}$. Carrier (i.e., barite) recycling during water treatment was shown to be effective in enhancing radium removal even after co-precipitation was completed. Calculations based on experimental results show that Ra levels in the precipitate generated in centralized waste treatment facilities far exceed regulatory limits for disposal in municipal sanitary landfills and require careful monitoring of allowed source term loading (ASTL) for technically enhanced naturally occurring materials (TENORM) in these landfills. Several alternatives for sustainable management of TENORM are discussed.

$$M^{2+} + SO_4^{2-} \rightarrow MSO_4 \qquad \text{(Precipitation)}$$

$$Ra^{2+} + MSO_4 \rightarrow M^{2+} + RaSO_4 \qquad \text{(Lattice Replacement)}$$

Equilibrium Constant:

$$Keq = \frac{[M^{2+}][RaSO_4]}{[Ra^{2+}][MSO_4]} = \frac{K_{sp,RaSO4}}{K_{sp,MSO4}}$$

Distribution Coefficient:

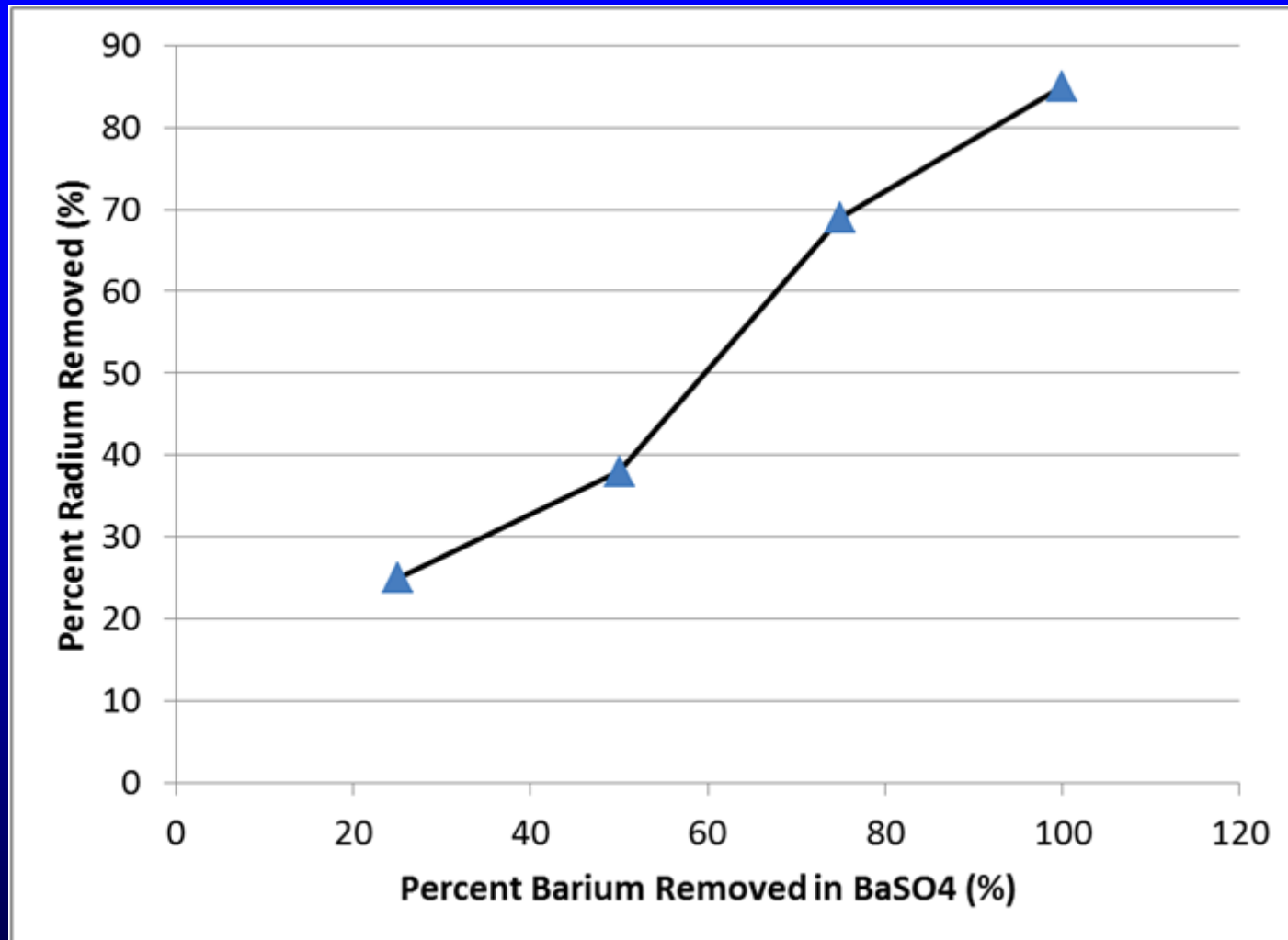$$Kd = \frac{M^{2+}}{Ra^{2+}} \frac{RaSO_4}{MSO_4}$$

Then,

$$Kd = \frac{K_{sp,RaSO4}}{K_{sp,MSO4}} \frac{\Upsilon_{Ra^{2+}}}{\Upsilon_{M^{2+}}} \frac{\Upsilon_{MSO4}}{\Upsilon_{RaSO4}}$$

For Ra-$BaSO_4$ co-precipitation, Kd=1.54.

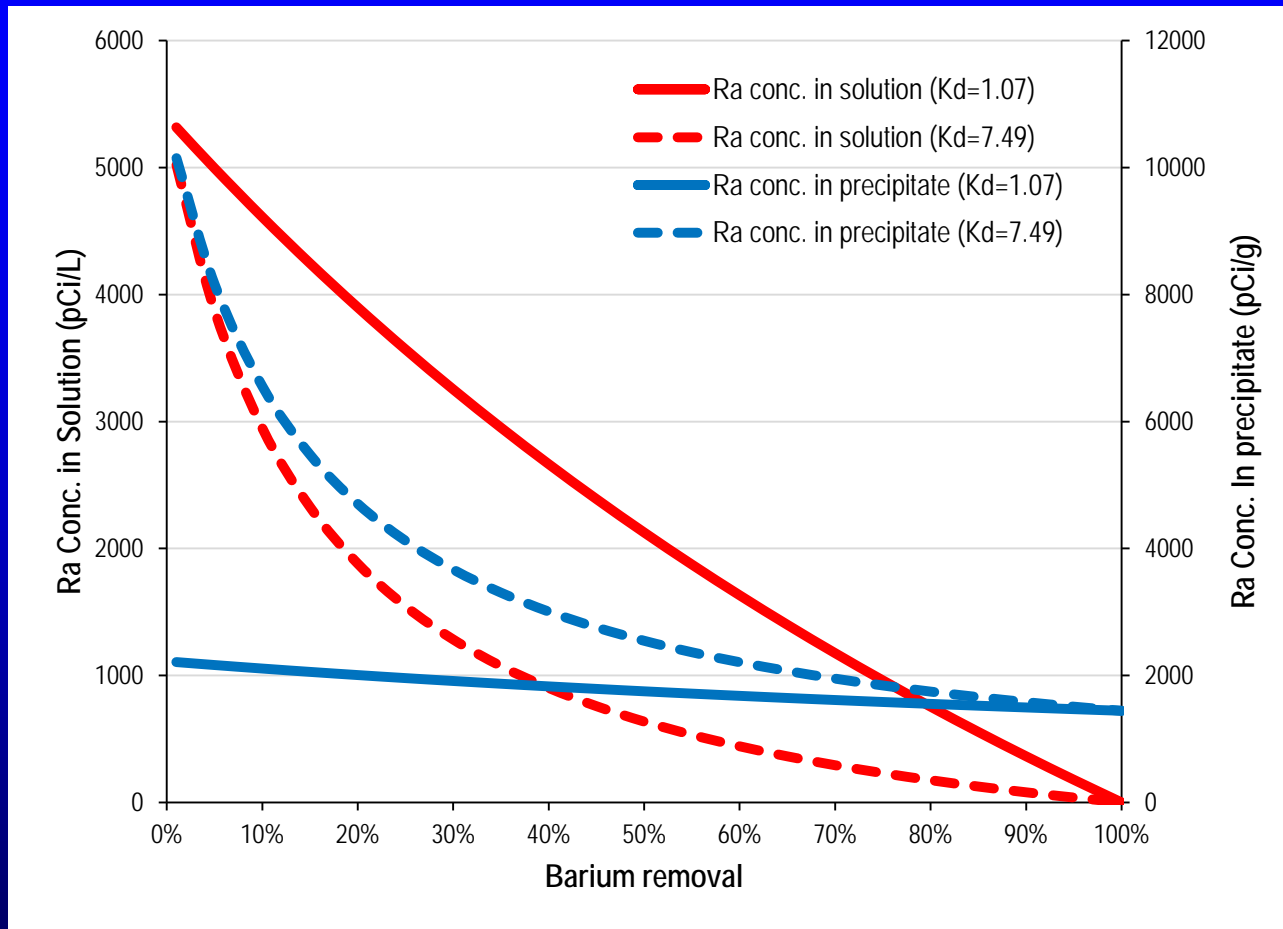Experimental results show Kd ranging from 1.07 – 7.49.

# Radium removal during precipitation



Radium is incorporated into $BaSO_4$ by coprecipitation / adsorption

# Ra in solid waste generated by CWT facility



Ra content is significantly higher than the landfill disposal limit of 25 pCi/g

Theoretical calculation of Radium concentration in solution and solid waste generated by sulfate precipitation

$[Ra^{2+}]_0 = 5,400$ pCi/L, $[Ba^{2+}]_0 = 2,200$ mg/L.

# Reuse of Solid Waste



## Recovery of BaSO$_4$

- Recovery of almost pure barite from the sedimentation tank

Ra-226 is incorporated into BaSO$_4$ by coprecipitation/adsorption

## Reuse of BaSO$_4$

- Must meet the API standards for drilling mud formulation

| Requirement for barite reuse | Standard |
|---|---|
| Density | > 4.1 g/cm$^3$ |
| Water-soluble alkaline earth metals (as Ca) | < 250 mg/kg |
| Residue larger than 75 µm | < 3.0% |
| Particles smaller than 6 µm | < 30% |

# Pilot Scale Test in NE PA
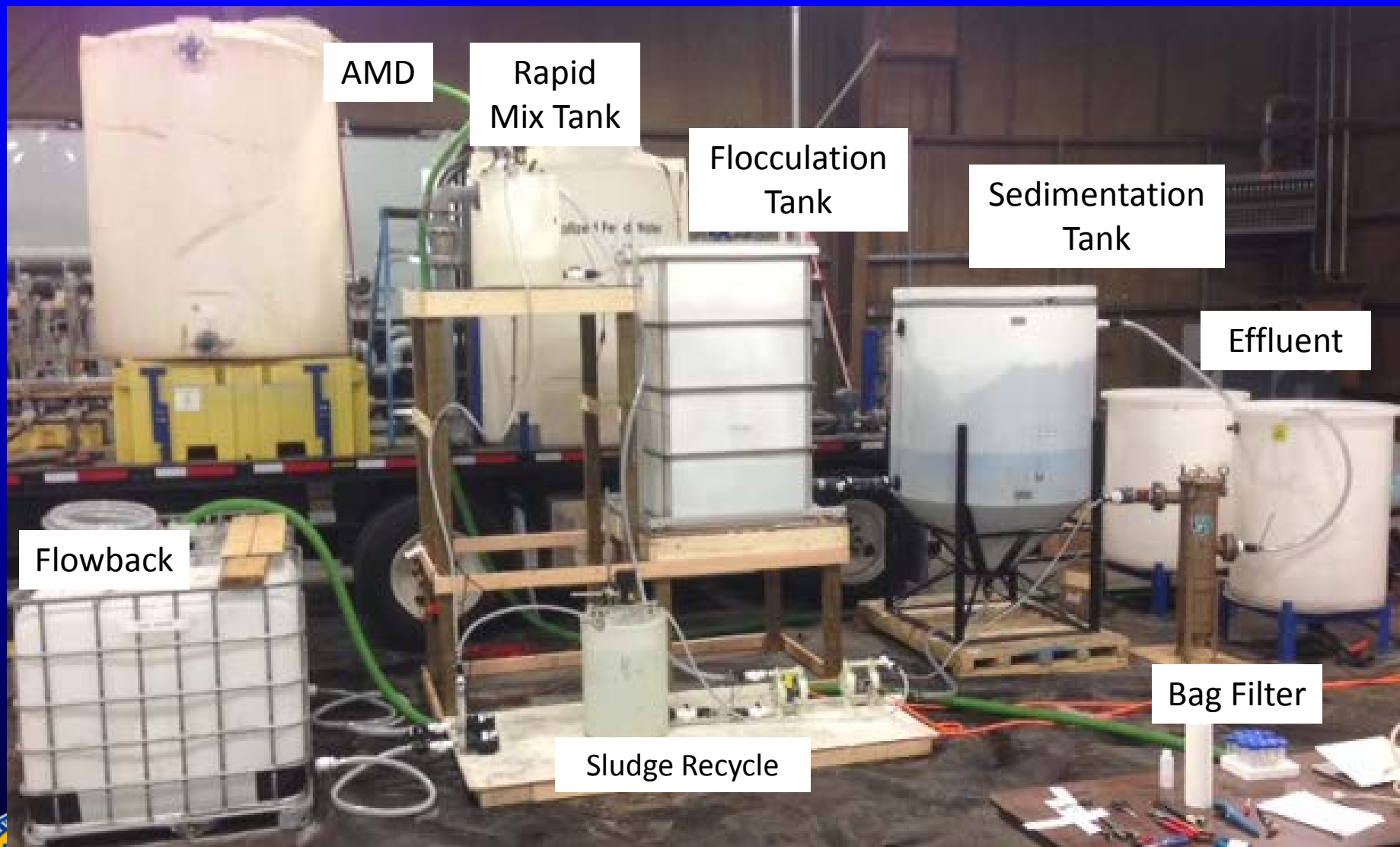
AMD    Flowback

**Influent**

| Parameter | FB | AMD |
|---|---|---|
| pH | 6.2 | 2.6 |
| TDS (mg/L) | 260,000 | 1,200 |
| $Ba^{2+}$ (mg/L) | 19,100 | - |
| $Sr^{2+}$ (mg/L) | 16,200 | - |
| $Fe_{dissolved}$ (mg/L) | 28.2 | 35.6 |
| Ra-226 (pCi/L) | 15,600 | - |
| $SO_4^{2-}$ (mg/L) | - | 1,150 |

**Effluent**

| Parameter | Value |
|---|---|
| pH | 7.4 |
| Turbidity (NTU) | < 3 |
| $Fe_{dissolved}$ (mg/L) | 0.1 |
| Ra-226 (pCi/L) | < 60 |
| $SO_4^{2-}$ (mg/L) | 75 |

Treated Water (waste)

# Controlling the Growth of Particles
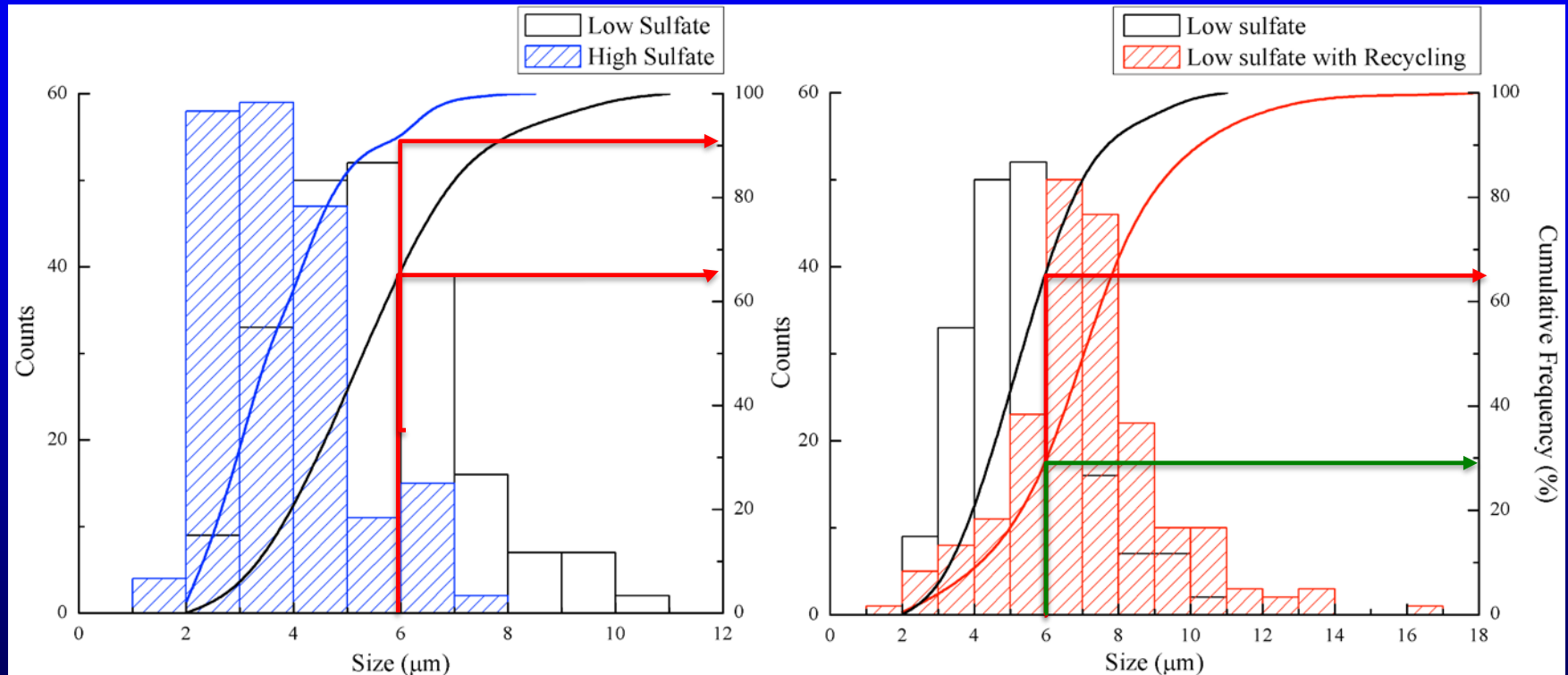


Impact of Sulfate Concentration

Impact of Sludge Recirculation

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# Thank You for Your Attention


# Questions?