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Bureau of Abandoned Mine Reclamation

Reducing Fresh Water Consumption in Hydraulic Fracturing by using Acid Mine Drainage as a Make-up Fluid

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33RD Annual Meeting of the American Society of Mining & Reclamation (ASMR)
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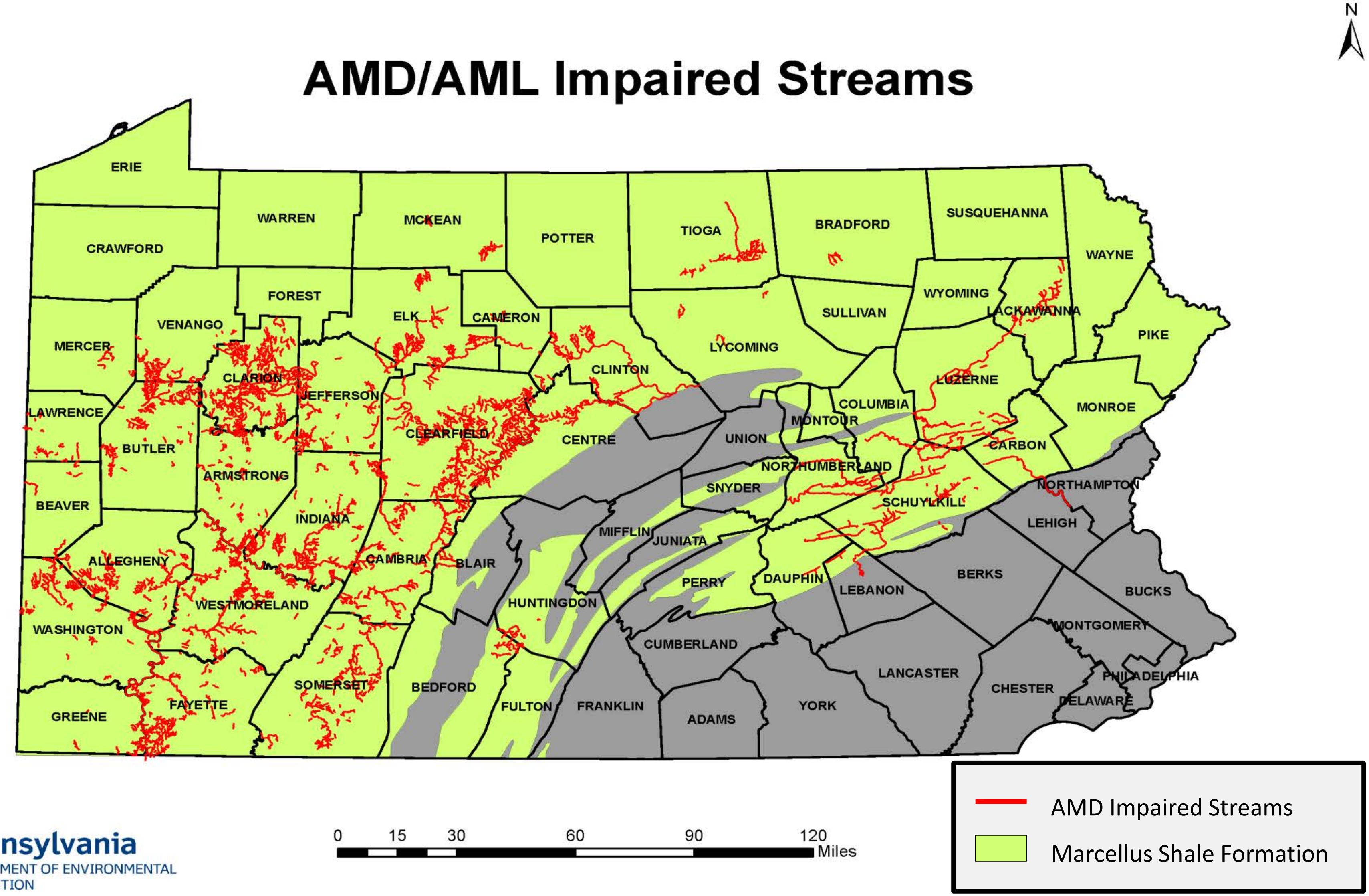
Limits of Marcellus Shale and AMD Impacted Streams in Pennsylvania



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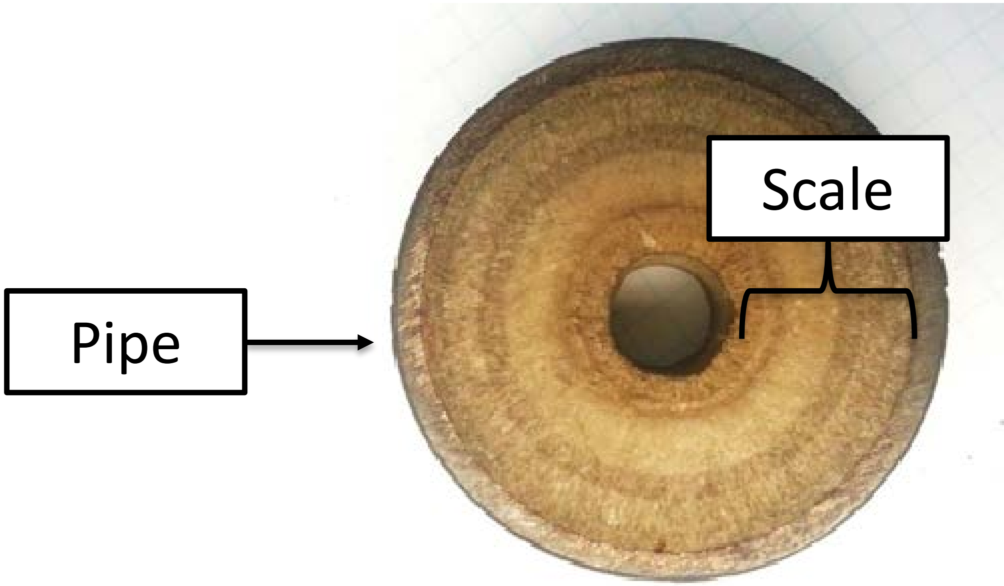
Marcellus Well – Westmoreland County PA

Aerial View of Hydraulic Fracturing Operation

Why is AMD not used?



- AMD Sulfate concentration usually >100 mg/L
- Will react with dissolved metals in well and form scale

Flowback

- Flowback is water that is produced within the first 30 days of production
- Contains high amounts of dissolved metals such as Barium and Strontium
- Companies would prefer to recycle this fluid for future wells

Can Two Negatives Result in Positive?

- (-) AMD has high sulfate concentration
- (-) Recycling flowback requires barium and strontium to be removed
- **(+)** Mix fluids to precipitate Barite and Celestite on surface

$$BaSO_4(s) \longleftrightarrow Ba^{2+} + SO_4^{2-} \qquad k_{eq}(-8.43)$$

$$SrSO_4(s) \longleftrightarrow Sr^{2+} + SO_4^{2-} \qquad k_{eq}(-5.17)$$

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Hypotheses

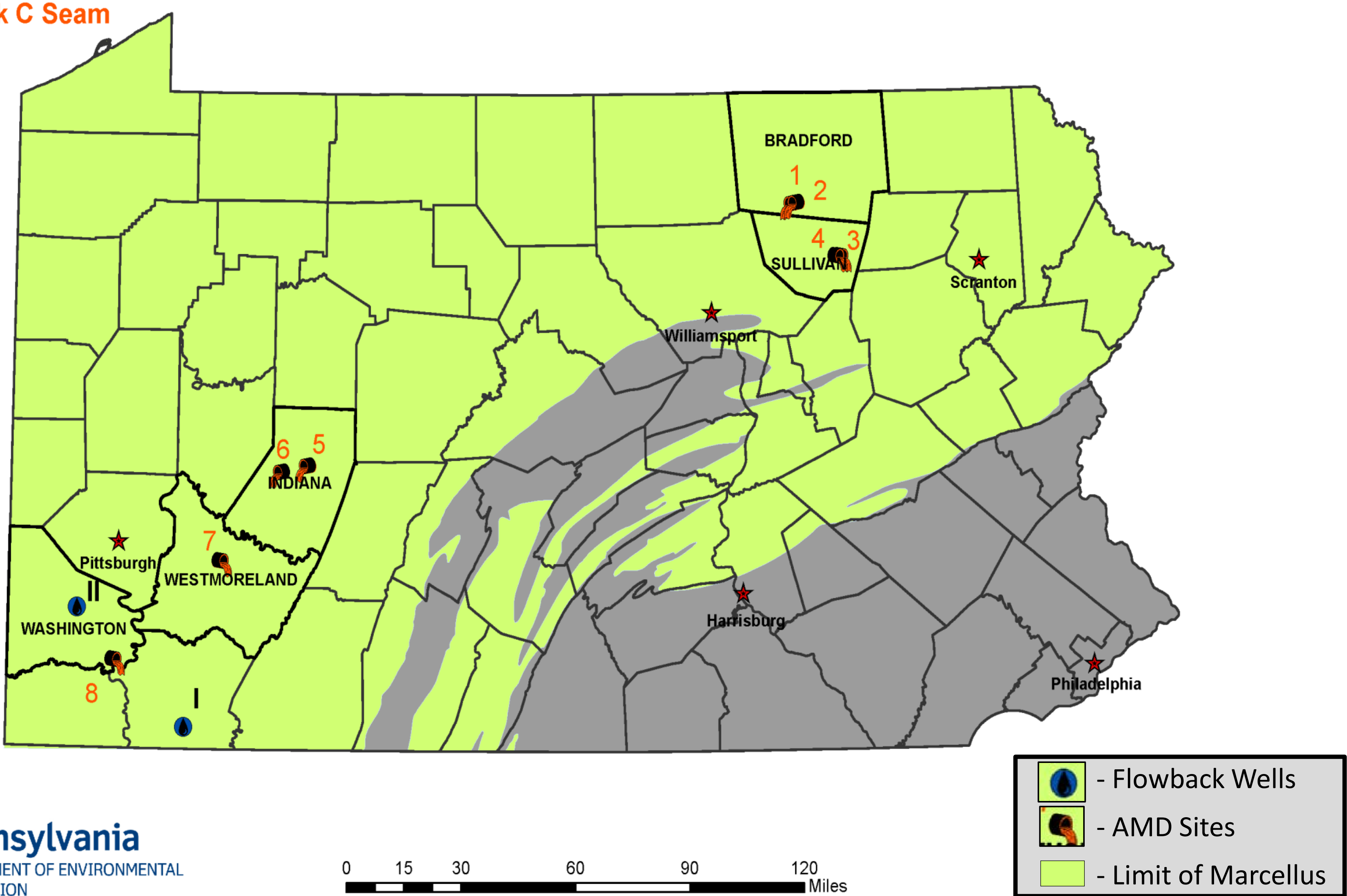
- Could mine drainage from abandoned mines be used as the make-up fluid as opposed to using freshwater sources?

- By mixing mine drainage with gas well flowback water could beneficial reactions be promoted which could make the flowback more suitable for recycling and less costly than by mixing it with freshwater?

Limits of Marcellus Shale Formation, Mine Drainage Discharge Locations, and Flowback Well Locations

AMD Discharge Key

1 - Long Valley Run
2 - Falls Creek
3 - Loyalsock B Seam
4 - Loyalsock C Seam
5 - Tanoma
6 - Ernest
7 - Crabtree
8 - Clyde



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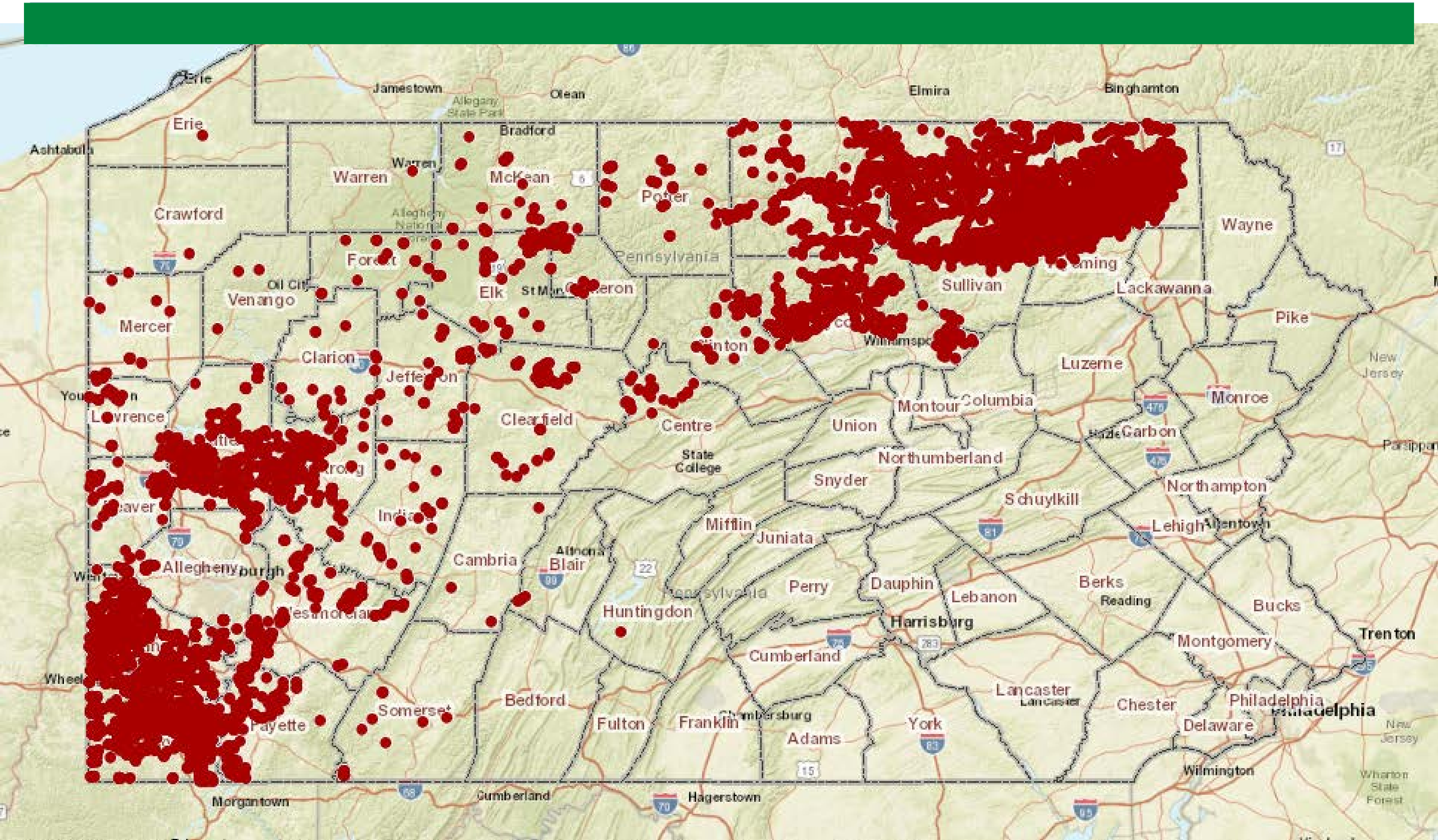
Marcellus Shale Wells Drilled in Pennsylvania (As of May 16, 2016)



C Vein Discharge – Sullivan County

Tanoma Discharge – Indiana County

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Ernest Discharge – Indiana County

Crabtree Discharge – Westmoreland County

Clyde Discharge – Washington County

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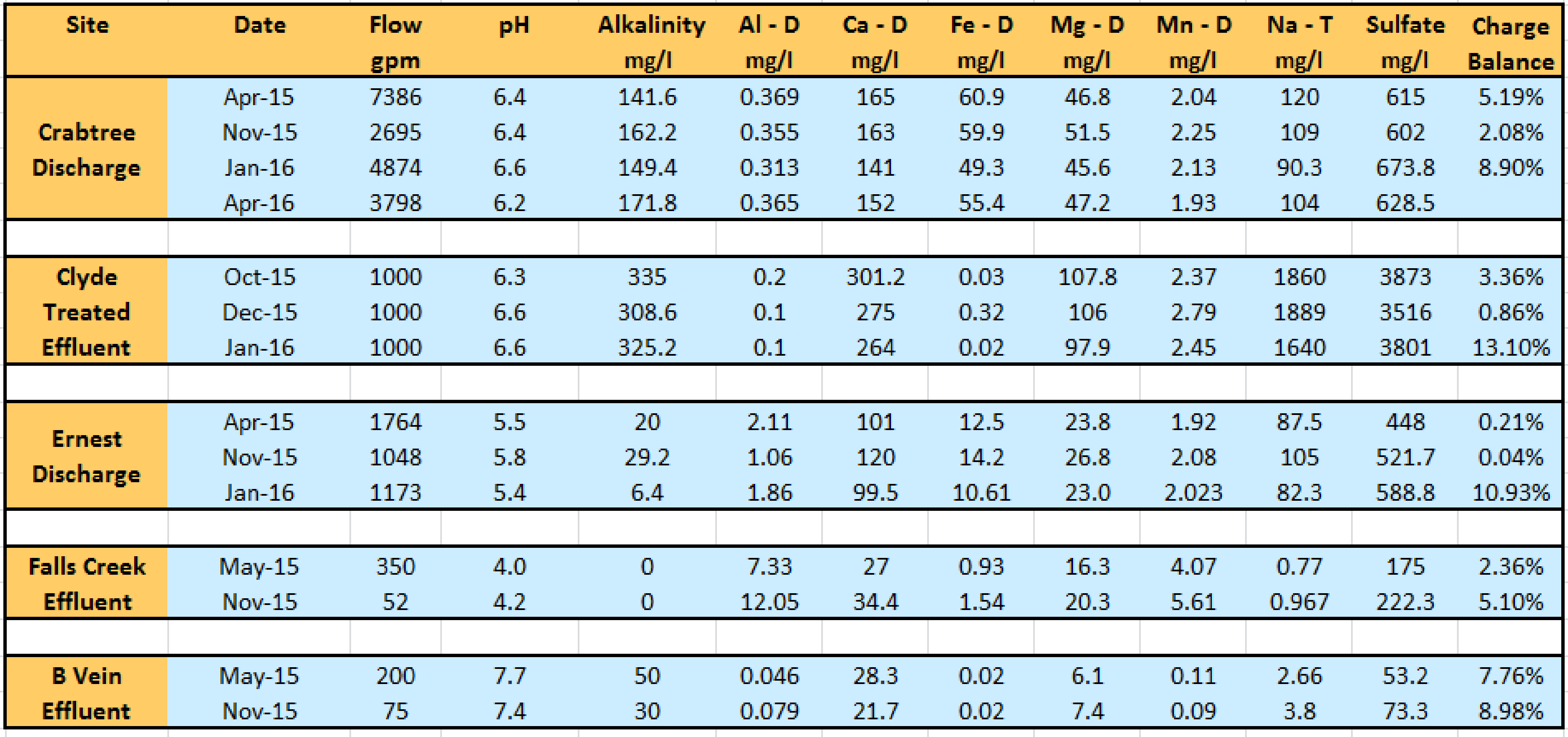
Field Sampling and Characterization of AMD and Flowback Waters

- **Field determinations of pH, Eh, Temp, Alkalinity and measured flows were obtained at all the AMD discharge sites**
- **The AMD discharges and flowback wells were sampled and sent to the PA DEP lab in Harrisburg, PA for analysis**
- **Total and dissolved analysis of all major cations, anions and trace elements associated with both mine drainage and flowback were performed**

Parameter	Analysis Method	Test Method
pH, Alkalinity	Titration	SM 4500 H-B, SM 2320B
Chloride, Sulfate	Colorimetric	SM 4500 CL-E, EPA 375.2
Bromide	IC	EPA 300
All other Metals	ICPMS	EPA 200.7

AMD Site Variability



Site	Date	Flow gpm	pH	Alkalinity mg/l	Al - D mg/l	Ca - D mg/l	Fe - D mg/l	Mg - D mg/l	Mn - D mg/l	Na - T mg/l	Sulfate mg/l	Charge Balance
Crabtree Discharge	Apr-15	7386	6.4	141.6	0.369	165	60.9	46.8	2.04	120	615	5.19%
	Nov-15	2695	6.4	162.2	0.355	163	59.9	51.5	2.25	109	602	2.08%
	Jan-16	4874	6.6	149.4	0.313	141	49.3	45.6	2.13	90.3	673.8	8.90%
	Apr-16	3798	6.2	171.8	0.365	152	55.4	47.2	1.93	104	628.5	
Clyde Treated Effluent	Oct-15	1000	6.3	335	0.2	301.2	0.03	107.8	2.37	1860	3873	3.36%
	Dec-15	1000	6.6	308.6	0.1	275	0.32	106	2.79	1889	3516	0.86%
	Jan-16	1000	6.6	325.2	0.1	264	0.02	97.9	2.45	1640	3801	13.10%
Ernest Discharge	Apr-15	1764	5.5	20	2.11	101	12.5	23.8	1.92	87.5	448	0.21%
	Nov-15	1048	5.8	29.2	1.06	120	14.2	26.8	2.08	105	521.7	0.04%
	Jan-16	1173	5.4	6.4	1.86	99.5	10.61	23.0	2.023	82.3	588.8	10.93%
Falls Creek Effluent	May-15	350	4.0	0	7.33	27	0.93	16.3	4.07	0.77	175	2.36%
	Nov-15	52	4.2	0	12.05	34.4	1.54	20.3	5.61	0.967	222.3	5.10%
B Vein Effluent	May-15	200	7.7	50	0.046	28.3	0.02	6.1	0.11	2.66	53.2	7.76%
	Nov-15	75	7.4	30	0.079	21.7	0.02	7.4	0.09	3.8	73.3	8.98%

- **Site specific seasonal variations in both flow and chemistry**
- **Regional quality differences – Anthracite vs. Bituminous sites**
- **Mine pool hydrology – flooded vs free draining**
- **Time since mining completion**

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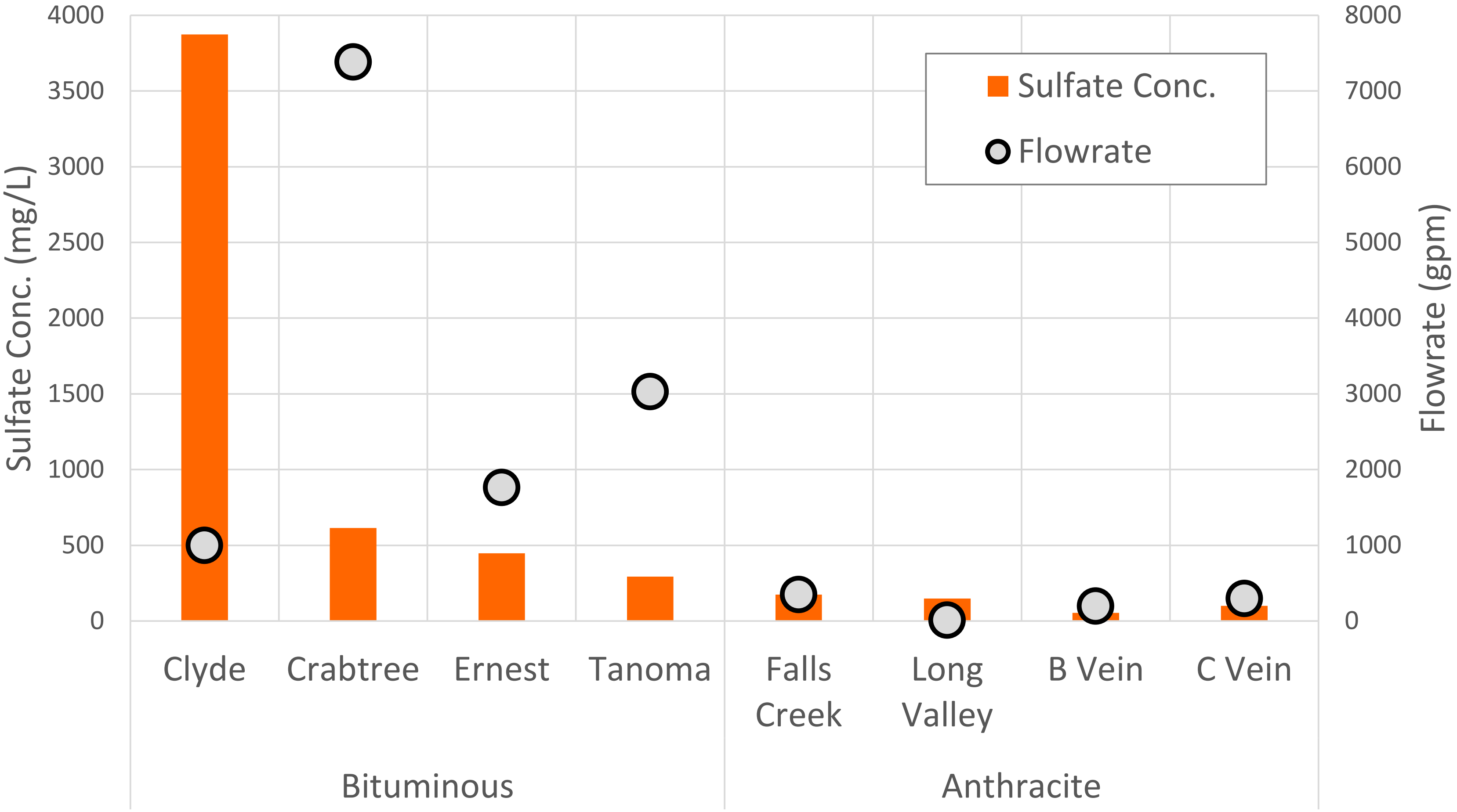
AMD Site Variability



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AMD Site Temporal Changes – Clyde Mine Pool

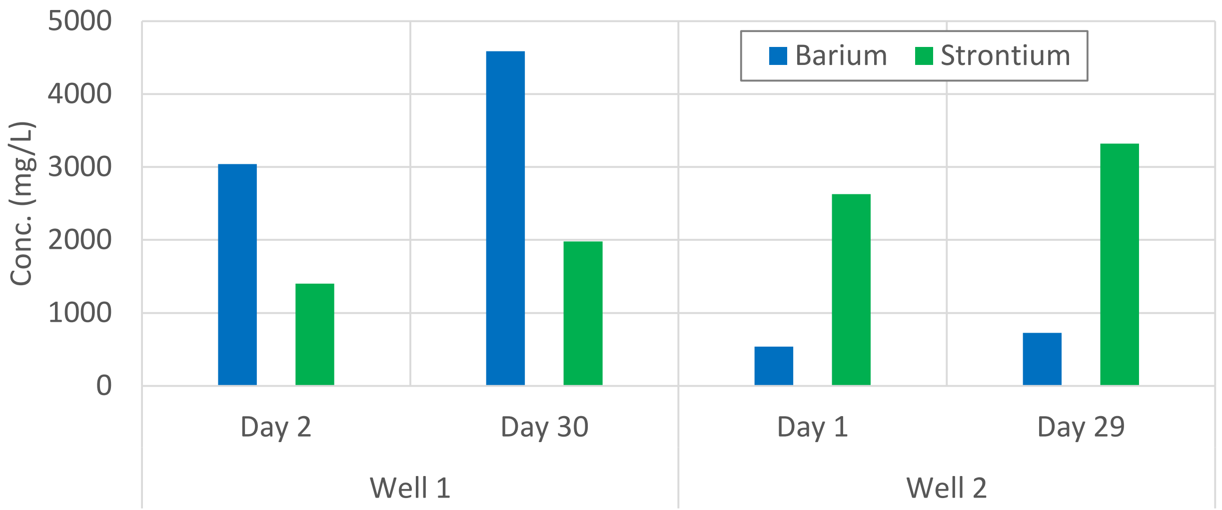
Date	pH	Alkalinity	Acidity	Fe	Mn	Al	Sulfate
1/24/2000	6.4	500	154	>300	8.47	0.56	6,085
5/15/2002	6.4	514	- 42	248	4.61	0.48	5,400
6/21/2005	6.3	519	- 23	213	4.32	< 0.2	4,350
1/6/2011	6.4	520	- 203	194	3.34	< 0.2	4,010
10/6/2014	6.4	550	-200	190	3.5	<0.2	4,000
5/15/2015	6.6	510	-240	154	2.6	<0.2	3,989
1/19/2016	6.6	520	-260	148	2.6	<0.2	3,593

All values except pH expressed as mg/l

- From 2000 to 2016
  - ~ 50 percent reduction in dissolved iron
  - ~ 70 percent reduction in dissolved manganese
  - ~ 40 percent reduction sulfate

Early and Late Flowback Characterization

Location	pH	Alk. (mg/L)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Ba^{2+} (mg/L)	Sr^{2+} (mg/L)	Fe (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)
Well 1 (Day 2)	6.2	256	24790	6204	626	3040	1400	120	56025	262
Well 2 (Day 1)	6.4	63	35400	13300	1308	540	1980	42	91939	78
Well 1 (Day 30)	6.1	218	25880	8244	841	4590	1800	198	60357	ND
Well 2 (Day 29)	6.2	86	39500	15400	1616	728	3290	55	103061	ND



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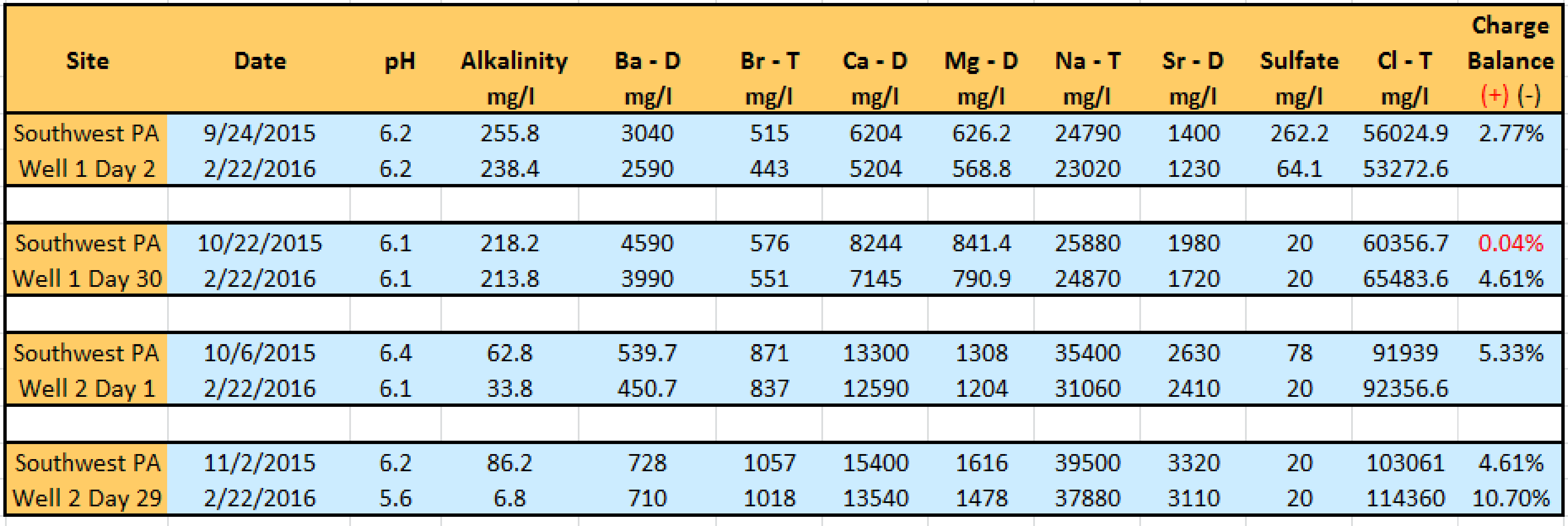
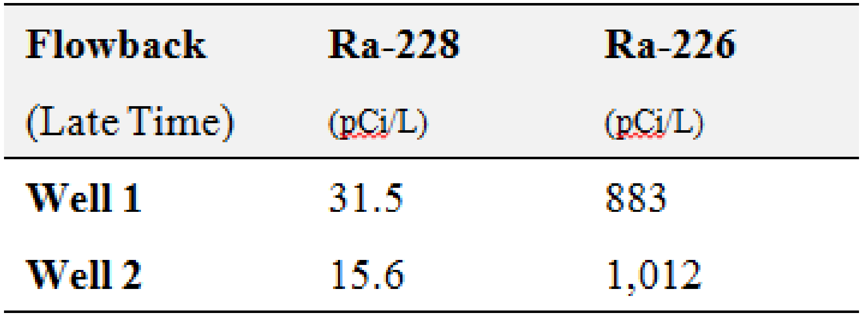
Flowback Water Chemistry



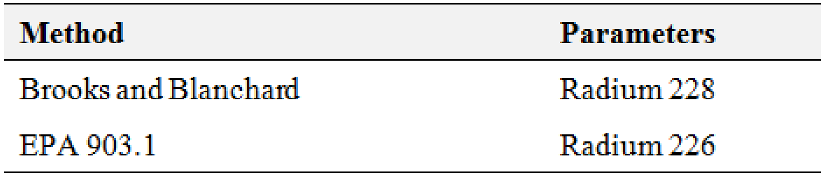
Site	Date	pH	Alkalinity mg/l	Ba - D mg/l	Br - T mg/l	Ca - D mg/l	Mg - D mg/l	Na - T mg/l	Sr - D mg/l	Sulfate mg/l	Cl - T mg/l	Charge Balance (+) (-)
Southwest PA Well 1 Day 2	9/24/2015	6.2	255.8	3040	515	6204	626.2	24790	1400	262.2	56024.9	2.77%
	2/22/2016	6.2	238.4	2590	443	5204	568.8	23020	1230	64.1	53272.6	
Southwest PA Well 1 Day 30	10/22/2015	6.1	218.2	4590	576	8244	841.4	25880	1980	20	60356.7	0.04%
	2/22/2016	6.1	213.8	3990	551	7145	790.9	24870	1720	20	65483.6	4.61%
Southwest PA Well 2 Day 1	10/6/2015	6.4	62.8	539.7	871	13300	1308	35400	2630	78	91939	5.33%
	2/22/2016	6.1	33.8	450.7	837	12590	1204	31060	2410	20	92356.6	
Southwest PA Well 2 Day 29	11/2/2015	6.2	86.2	728	1057	15400	1616	39500	3320	20	103061	4.61%
	2/22/2016	5.6	6.8	710	1018	13540	1478	37880	3110	20	114360	10.70%

- Flowback samples were re-analyzed after ~ 5 months hold time
  - Sulfate present in early flowback samples has precipitated
  - Significant changes in dissolved Ba, Br, Ca, Fe, Mg, Sr and total alkalinity

NORM Sampling



Flowback (Late Time)	Ra-228 (pCi/L)	Ra-226 (pCi/L)
Well 1	31.5	883
Well 2	15.6	1,012



Method	Parameters
Brooks and Blanchard	Radium 228
EPA 903.1	Radium 226

- Analysis reported as radioactivity units (pCi/L)
- Transformed to mass units by applying Specific Activity conversion formula
- Well 1 example: Ra ^{226} = 883 pCi/L would equate to a concentration of 8.92x10^{-7} mg/l
- Radium Sulfate formation would not be observable through analyzing changes in sulfate concentration

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Mixing Test Objectives

- Setting up mix tests
  - Normalized mixes to a ratios of (SO_4: Ba+Sr) = 1:1
  - This means that there is just enough sulfate to react with all barium and strontium in mix

- Measure Removal Efficiency
  - The goal was to remove 100% of the barium, strontium and sulfate

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Setting up Mixes

Mixture		Ratio	% AMD	% Flowback
Discharge	Well	(SO_4:Ba+Sr)	in mix	in mix
Clyde	Well 1 (E)	0.98	49%	51%
Clyde	Well 2 (E)	0.93	46%	54%
Clyde	Well 1 (L)	1.24	61%	40%
Crabtree	Well 1 (E)	1.05	86%	14%
Crabtree	Well 2 (E)	1.00	84%	16%
Crabtree	Well 1 (L)	1.43	91%	9%
Ernest	Well 1 (E)	1.23	89%	11%
Ernest	Well 2 (E)	1.18	88%	12%
Ernest	Well 1 (L)	1.30	91%	9%
Tanoma	Well 1 (E)	1.14	93%	7%
Tanoma	Well 2 (E)	1.09	92%	8%

Mix Test Results

Mixture		**Barite SI**	**Celestite SI**
Discharge	Well	Log(IAP/keq)	Log(IAP/keq)
Clyde	Well 1 (E)	3.7	0.0
Clyde	Well 2 (E)	2.8	0.1
Clyde	Well 1 (L)	3.9	0.1
Crabtree	Well 1 (E)	3.0	-0.7
Crabtree	Well 2 (E)	2.1	-0.6
Crabtree	Well 1 (L)	3.1	-0.7
Ernest	Well 1 (E)	3.1	-0.7
Ernest	Well 2 (E)	2.1	-0.7
Ernest	Well 1 (L)	3.1	-0.7
Tanoma	Well 1 (E)	2.7	-1.1
Tanoma	Well 2 (E)	1.8	-1.0

- SI = Saturation Index
- Basically, how far from equilibrium is the mineral
  - (+) precipitation
  - (-) dissolution
- $SI = \log_{10}\left(\frac{IAP}{K_{eq}}\right)$

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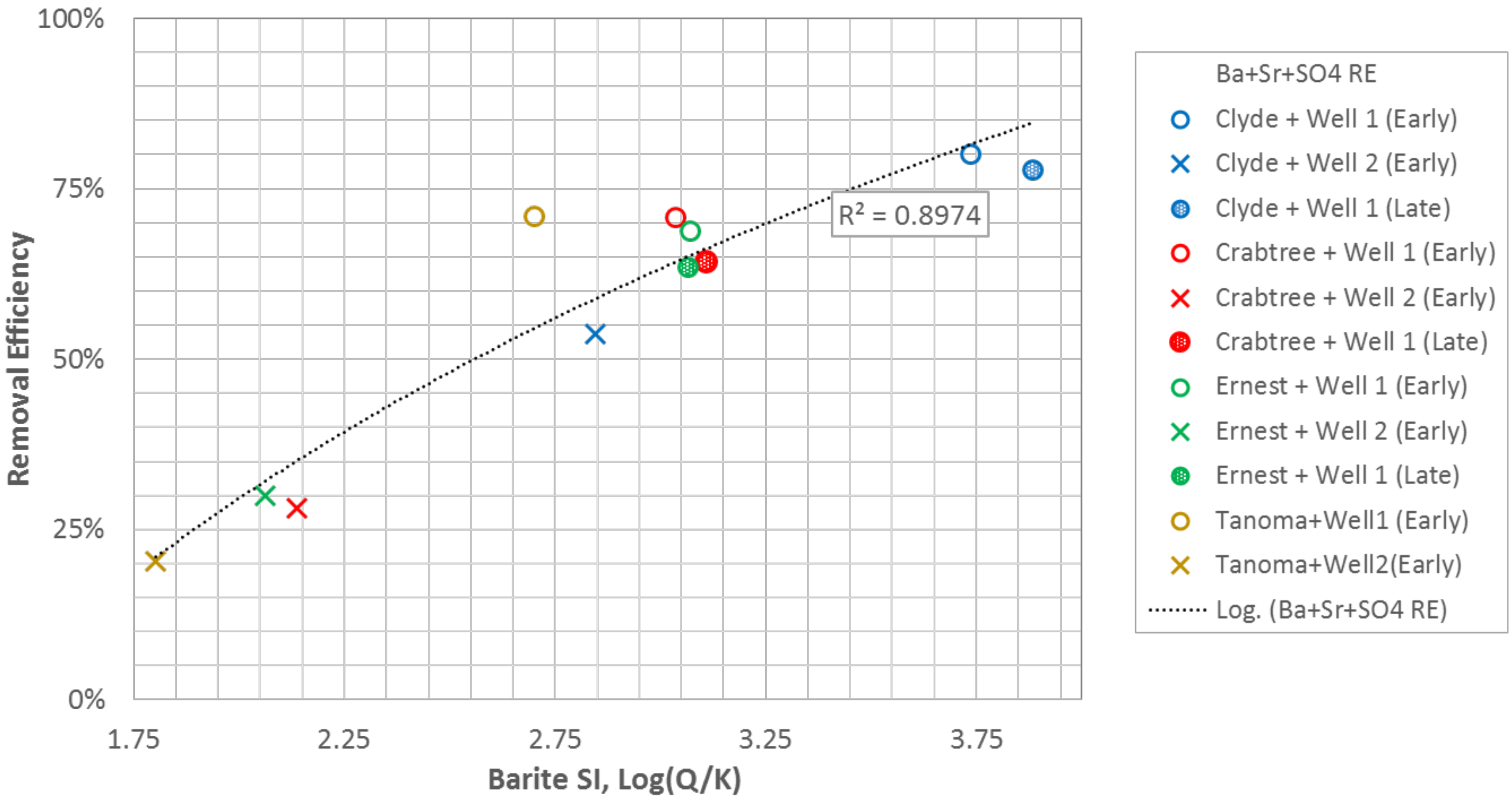
Mix Test Results

Mixture		**Barite SI**	**Celestite SI**	**Ba**	**Sr**	**SO_4**	**Total**
Discharge	Well	Log(IAP/keq)	Log(IAP/keq)	RE	RE	RE	RE
Clyde	Well 1 (E)	3.7	0.0	100%	53%	74%	**80%**
Clyde	Well 2 (E)	2.8	0.1	100%	46%	53%	**54%**
Clyde	Well 1 (L)	3.9	0.1	100%	41%	73%	**78%**
Crabtree	Well 1 (E)	3.0	-0.7	100%	32%	62%	**71%**
Crabtree	Well 2 (E)	2.1	-0.6	100%	18%	24%	**28%**
Crabtree	Well 1 (L)	3.1	-0.7	100%	14%	56%	**64%**
Ernest	Well 1 (E)	3.1	-0.7	100%	30%	60%	**69%**
Ernest	Well 2 (E)	2.1	-0.7	99%	15%	30%	**30%**
Ernest	Well 1 (L)	3.1	-0.7	100%	22%	51%	**63%**
Tanoma	Well 1 (E)	2.7	-1.1	100%	37%	62%	**71%**
Tanoma	Well 2 (E)	1.8	-1.0	93%	8%	19%	**20%**

Removal Analysis



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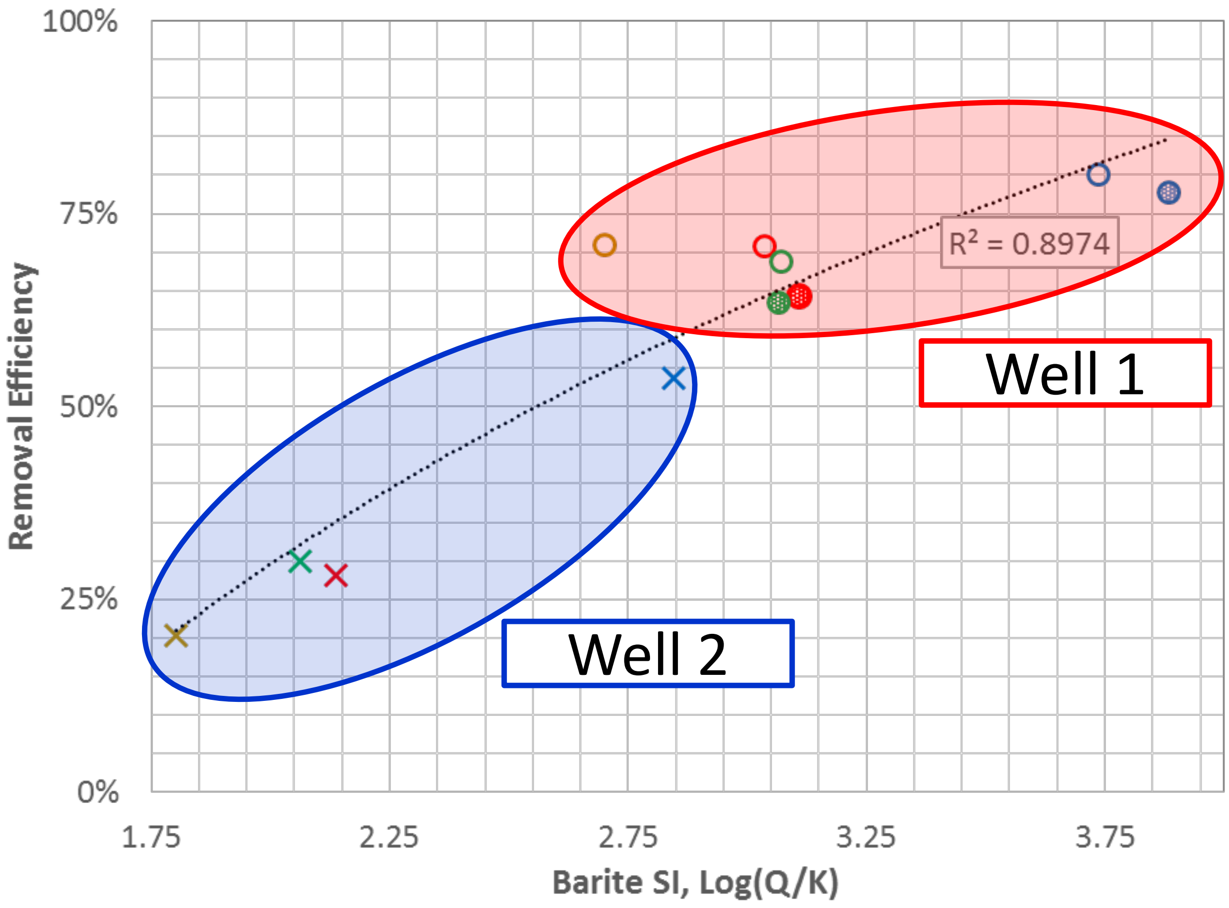
Well Composition Effect



Well 1

-Higher Barite SI

-Higher Removal Efficiency

Well 2

-Lower Barite SI

-Lower Removal Efficiency

	Ba^{2+} (mg/L)	**Sr^{2+}** (mg/L)
Well 1	3,040	1,400
Well 2	540	1,980

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XRD Analysis

→ Decreasing Mass % →

Mix	Mineral 1	Mineral 2	Mineral 3
Clyde + Well 1	$Ba_{75\%}Sr_{25\%}SO_4$	$Ba_{50\%}Sr_{50\%}SO_4$	$NaCl$
Clyde + Well 2	$Ba_{75\%}Sr_{25\%}SO_4$	$BaSO_4$	$NaCl$
Crabtree + Well 1	$Ba_{75\%}Sr_{25\%}SO_4$	$BaSO_4$	
Crabtree + Well 2	$NaCl$	$CaCl_2(H_2O)_4$	$BaSO_4$
Ernest + Well 1	$Fe_3(Si_2O_5)(OH)_4$	$NaCl$	FeS_2
Ernest + Well 2	$NaCl$	$BaSO_4$	

- Common minerals were:
  - Barium-Strontium Sulfate ($Ba_xSr_{1-x}SO_4$)
  - Barite ($BaSO_4$)
  - Halite ($NaCl$)
- But no Celestine ($SrSO_4$) in precipitate

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Discussion of Mixing Results

- Mixing Tests
  - For max removal of barium, strontium and sulfate, need to increase barite saturation index
  - Can be achieved using wells that have higher barium concentration than strontium

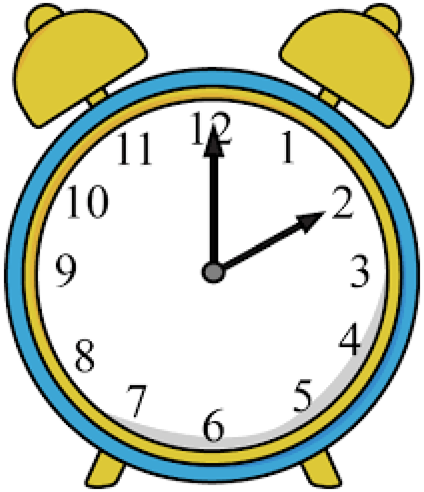
- XRD Analysis
  - “Dirty Minerals” form between barium and strontium
  - No celestite formation
  - Indicates that sulfate is not the best for removing strontium

Radium Removal

Mix	**Ratio** (SO4:Ba+Sr)	**AMD** in mix	**Flowback** in mix	**Ra 228** Removal	**Ra 226** Removal
Clyde Well 2 (L)	4.14	81%	19%	87%	100%
Crabtree Well 1 (L)	1.43	91%	9%	100%	100%
Ernest Well 2(L)	0.15	51%	49%	82%	96%

- Virtually all radium removed in a relatively small mass

Kinetic Testing



- For project to be economic, reactions must occur quickly
- Methodology
  - Measure pH, Alk., Ba, Ca, Sr, and SO_4 once a day for 14 days
- Goal
  - Determine how long samples must remain in contact to remove maximum amount

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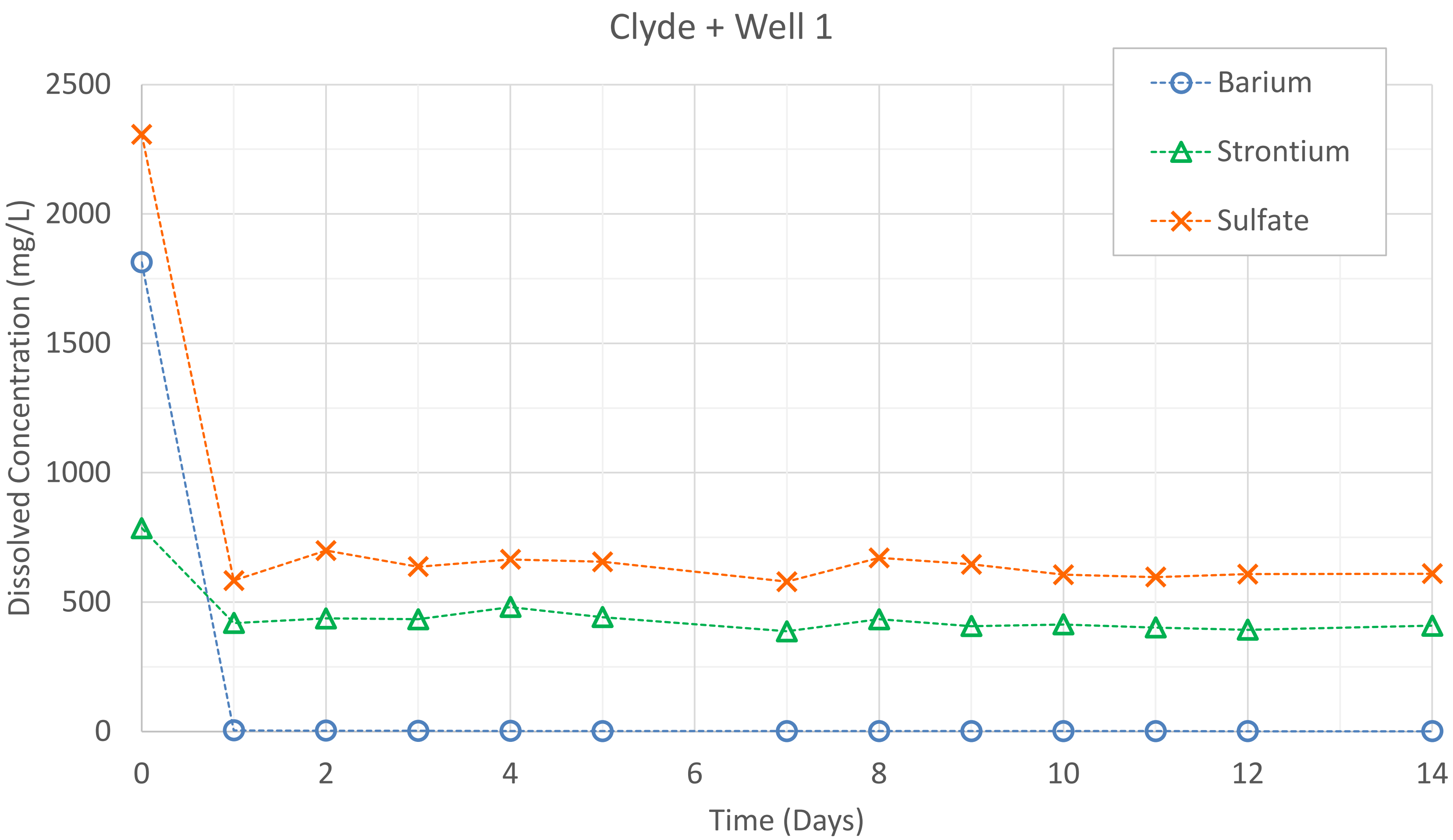
Kinetic Test Results



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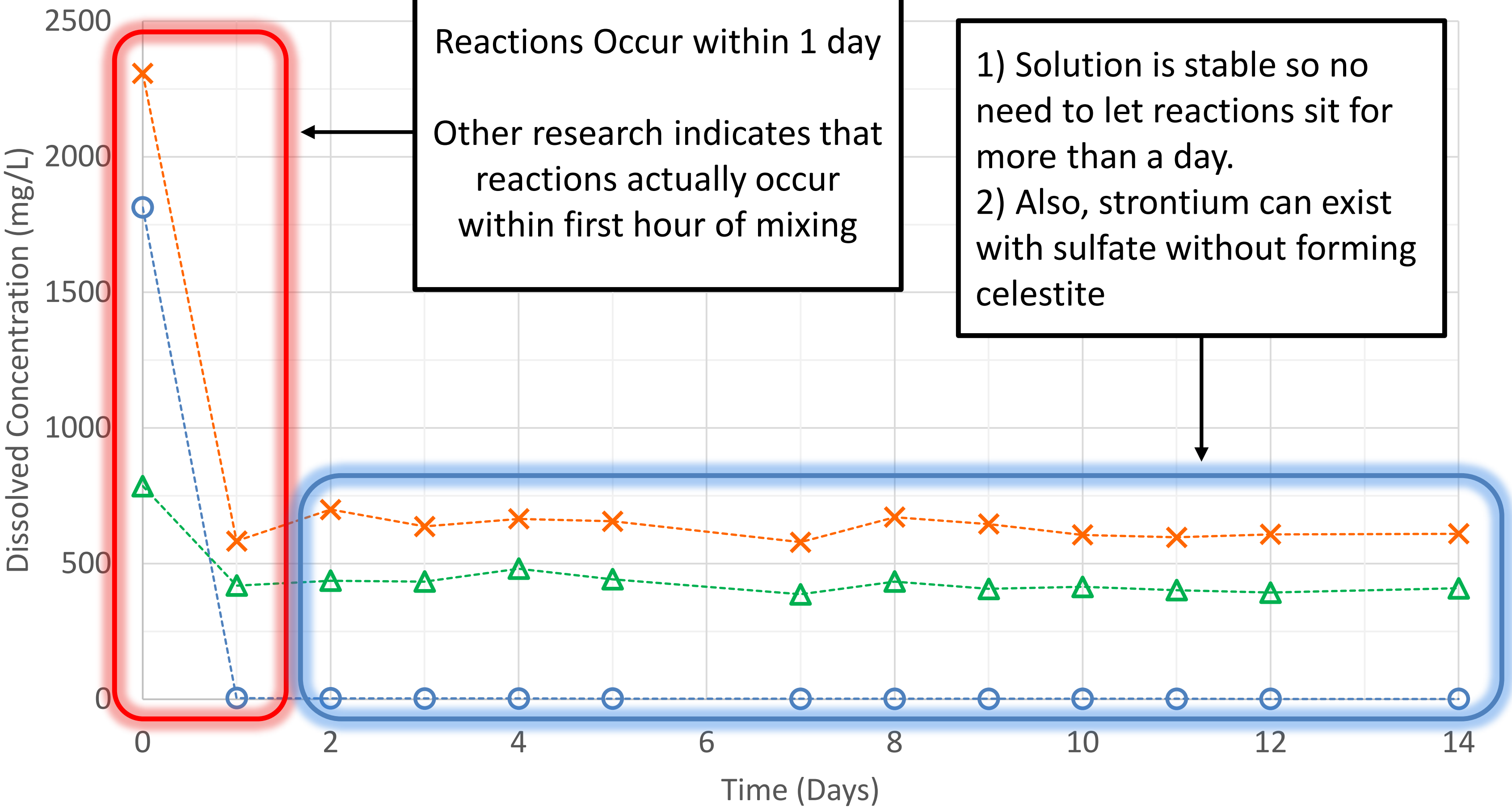
Discussion of Kinetic Test



Reactions Occur within 1 day

Other research indicates that reactions actually occur within first hour of mixing

1) Solution is stable so no need to let reactions sit for more than a day.
2) Also, strontium can exist with sulfate without forming celestite

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Conclusions

Goals

- For mixing test
  - ✓ Remove 100% barium
  - ✗ Remove 100% strontium
  - ✓ Sulfate levels <100 mg/L
- Kinetic Testing
  - ✓ Reaction occur fast

Learnings

- Celestite is not forming in mixture
- Rather, $Ba_xSr_{1-x}SO_4$ is forming
- Sulfate is not best removing agent for strontium

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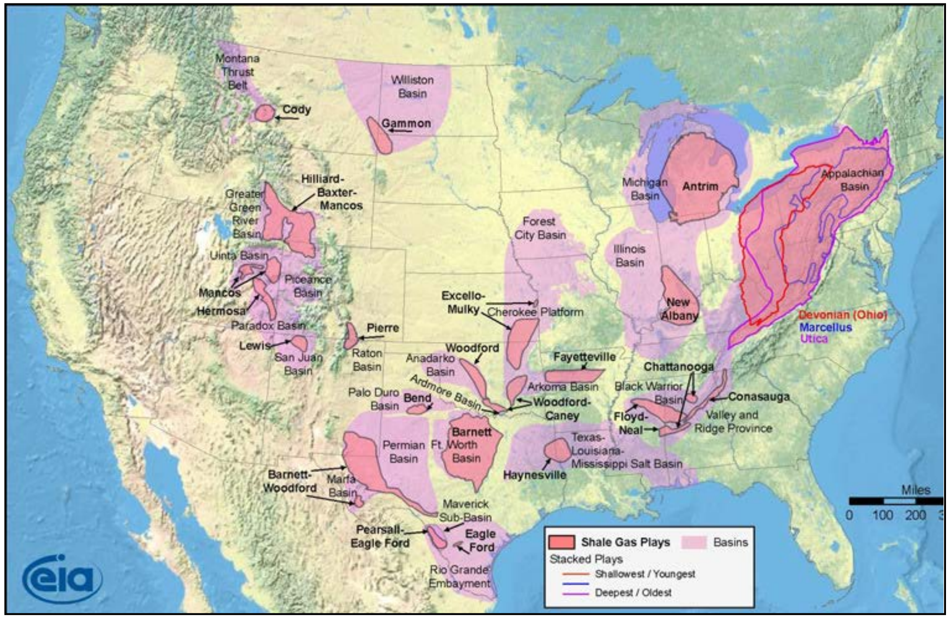
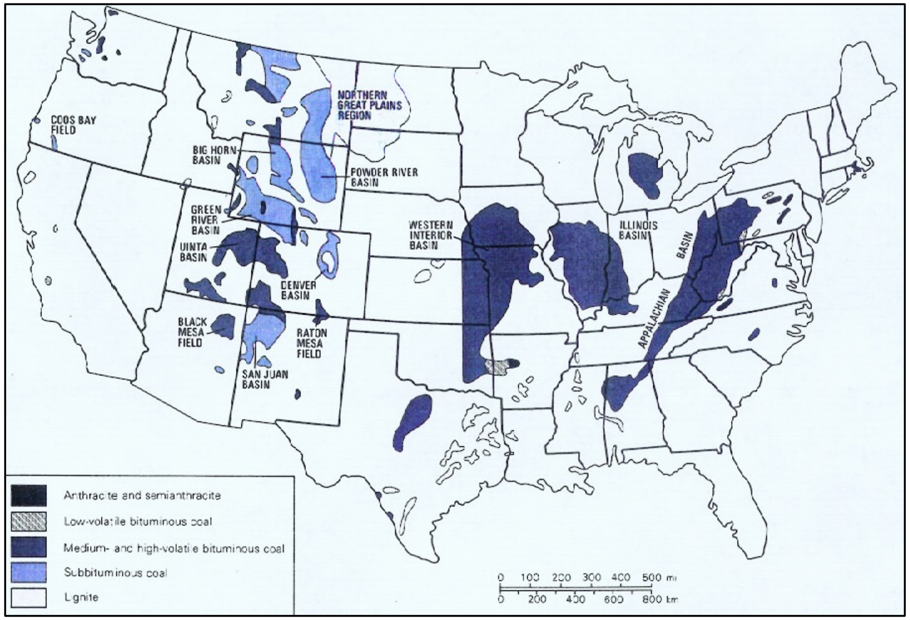
Future Work

- Currently modeling reactions
  - CrunchFlow (reactive flow and transport software)
  - Geochemists Workbench
- Determining mixing ratios to:
  - Remove 100% barium
  - Reduce sulfate to < 100 mg/L
- Reduce strontium using other means
  - Adding some alkaline mineral to increase the carbonate in the mix to potentially form strontianite ($SrCO_3$)

Applications





US Shale Gas Deposits

US Coal Basins

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Questions?

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