Evaluation of Appalachian Mine Spoil Leachate Chemistry and Its Associated Geochemical Influences

E.V. CLARK, W.L. DANIELS, Z. ORNDORFF, C.E. ZIPPER, AND K. ERIKSSON

ASMR 2015

Virginia Tech

Outline

- Overview of total dissolved solids (TDS)
- Methods
  - Column leaching
  - Mineralogical analysis
- Results
  - Patterns of Ion Release
  - Mineralogy
- Conclusions

Introduction

- >600,000 ha of land in Central Appalachia have been mined since the 1970's (Zipper et al. 2011)
- Overburden is comprised of many different rock types of different mineralogical compositions and weathering extents

Figure 1. An active surface mine in southwestern Virginia.

http://cnre.vt.edu/magazine/articles/201305/cover-front/powell-river-project.html

TDS Generation

- TDS=Total Dissolved Solids
- Exposing previously buried rock materials to ambient conditions causes rapid weathering via:
  - Sulfide oxidation

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$
$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \quad (2)$$
$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \quad (3)$$
$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

  - Carbonate dissolution (simplified)

    $H_2O + CO_2 = H_2CO_3$

    $CaCO_3 + H_2CO_3 = Ca^{+2} + 2HCO^-_3$

  - Hydrolysis of feldspars
    - $2KAISi_3O_8 + 2H^+ + 9H_2O \rightarrow H_4Al_2Si_2O_9 + 4H_4SiO_4 + 2K^+$

      (Orthoclase) (Water) (Kaolinite) (Silicic Acid)

TDS in Streams

- Precipitation events cause water to move through the spoil materials and eventually discharge into a stream
  - TDS can be approximated by measuring electrical conductivity (EC)

Figure 2. Mine spoil fill discharge in southwestern Virginia. Photo courtesy of Dan Evans.

Why do we care about TDS?

- "Saltier" stream water relative to reference streams
  - Elevated Ca, Mg, K, Sulfate, Bicarbonate
- Multiple studies have shown that there is biological community impairment at 300- 500 µS/cm (Pond et al., 2008; Cormier et al., 2013; Timpano et al., 2015)
- Mining companies are trying to understand the drivers of TDS release and how to mitigate it

Project Objectives

1. Describe patterns of ion release from Central Appalachian mine spoils placed in leaching columns
2. Investigate mineralogical influences on Central Appalachian mine spoil leachate chemistry

Methodology

Methods

- 34 mine spoil samples have been collected from Central Appalachia (KY, WV, VA)
- Geology
  - Pennsylvanian aged (~ 300 million years old) Pottsville Group
    - Sandstones, interbedded shales, mudstones

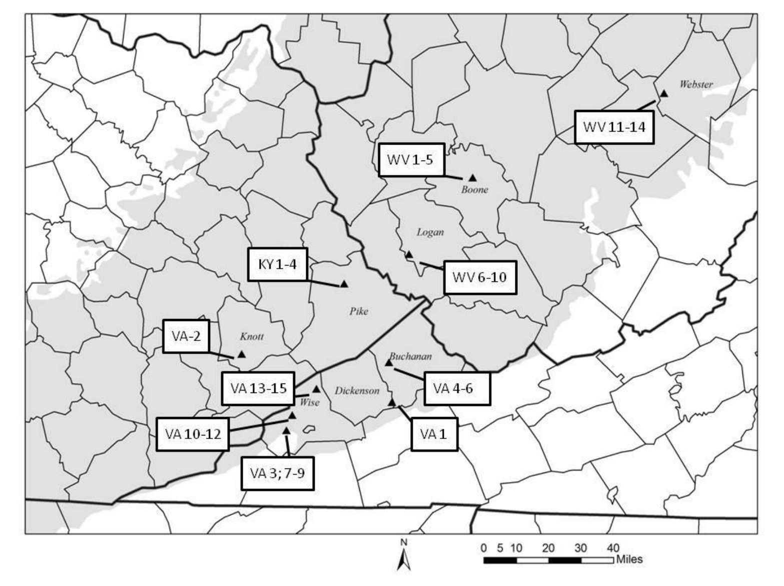


Figure 3. Location map of collected mine spoils.

Methods

- Spoil Data Set
  - 15 WV, 4 KY, 15 VA samples
  - 5 weathered, 22 unweathered, 6 mixed
  - 2 black shales, 8 mixed, 8 mudstones, 16 sandstones
- Use leaching columns: provide best approx. of field weathering conditions (Caruccio et al. 1993)

Methods

1. Air dry, crush and sieve (1.25 cm diameter)
2. Columns= 40 cm tall with 7.4 cm diameter
3. Pack column-fill with 27 cm of spoil
4. Apply simulated rainfall (pH=4.6) at 125 mL (2.54 cm) events and collect leachate
   - Done 2x a week for 20 weeks 40 total leaches (Leach 0-39)

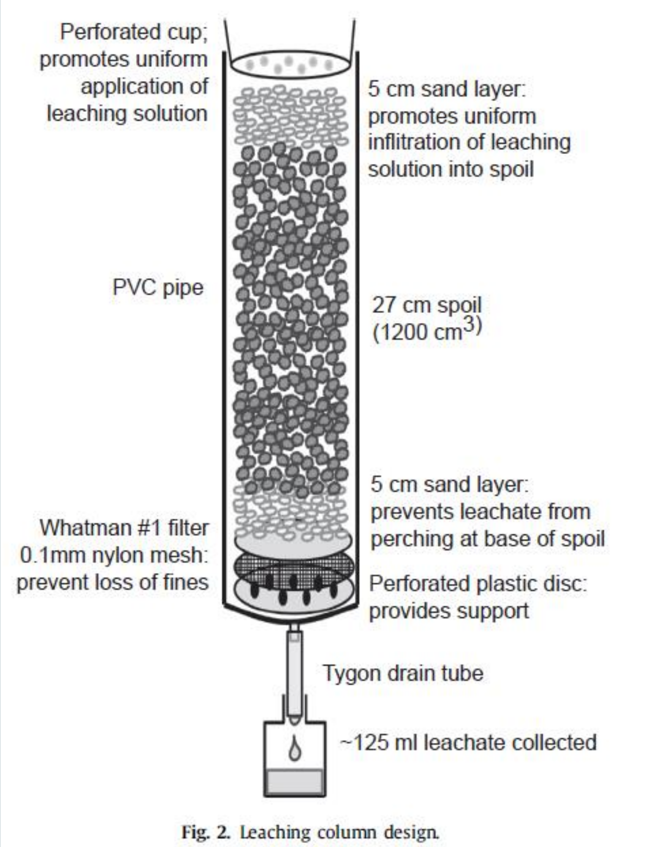


Figure 4. Diagram of the leaching column set up (From Orndorff et al., 2015).

Methods

- Ions Analyzed: Al, As, Ca*, Cd, Cl, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se, Zn, Sulfate, Bicarb
  - Ion Concentration: EPA method SW 846 6020A and a Thermo Electron Corporation ICP-MS
  - Sulfur: EPA method SW 846 6010B and a Spectro ARCOS ICPES Model FHS16 (S was then converted to sulfate)
  - Inorganic Carbon: Shimadzu TOC analyzer (IC converted to bicarbonate)

*Ca, K, Mg, Na, Sulfate and Bicarb release patterns are described in Orndorff et al. (2015)

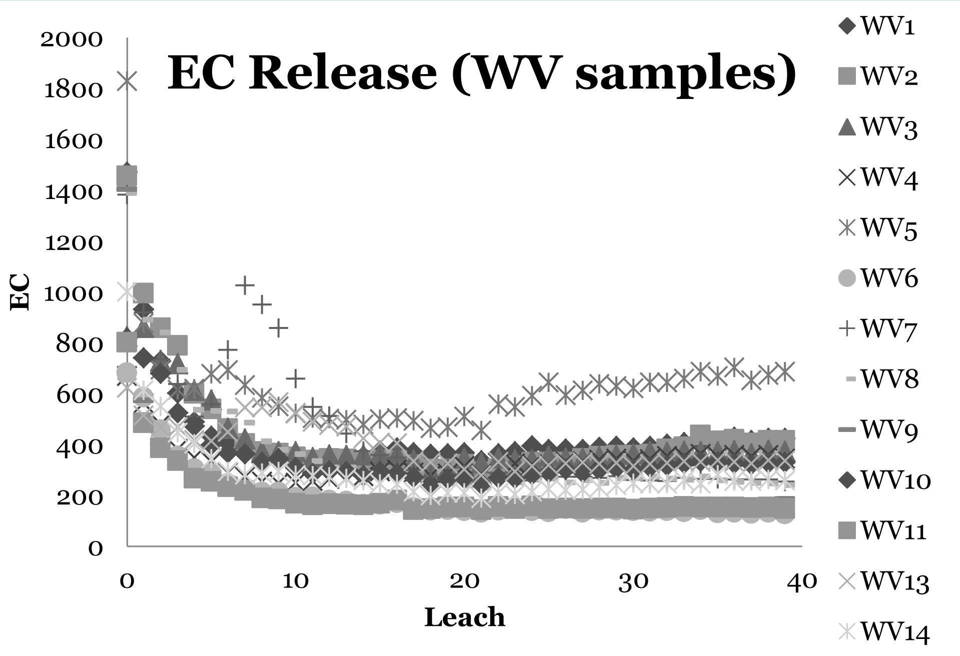
Methods

- Mineralogy
  - 48 thin sections (30 um thick) were prepared and analyzed via petrographic microscopy (by K. Eriksson-VT GEOL)
    - Mineral abundances (abundant, common, or rare)
    - Mineral point counts (~400 counts per slide)
    - Microprobe analysis of feldspars

Results

TDS Leaching Patterns

- EC generally declines quickly (within 5-10 leaches) then become stable over time



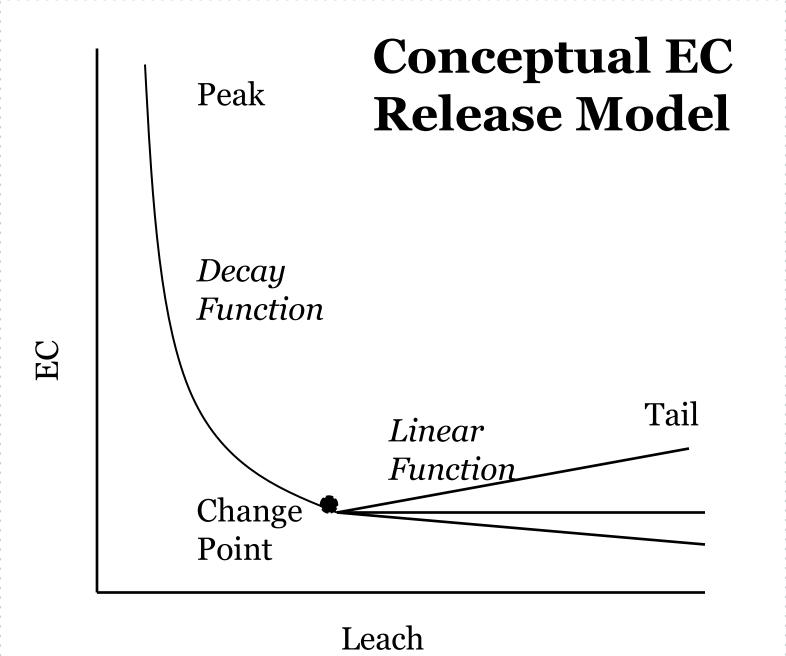


Figure 5. Typical EC release patterns from collected mine spoils (left) and conceptualized model of EC release (right).

Classification of Ion Leaching Behavior

- 5 classes (for all ions except bicarbonate)
  1. Decreases quickly to change point, then decreases or remains constant (may have some outliers in tail)
     - ALL Cl, Cu, Na, Ni, and Sulfate
     - Majority of Al, Ca, K, Mg, Mn, Se
  2. Decreases quickly to change point, then increases in linear component
     - Only occurs for Mg in 5 samples

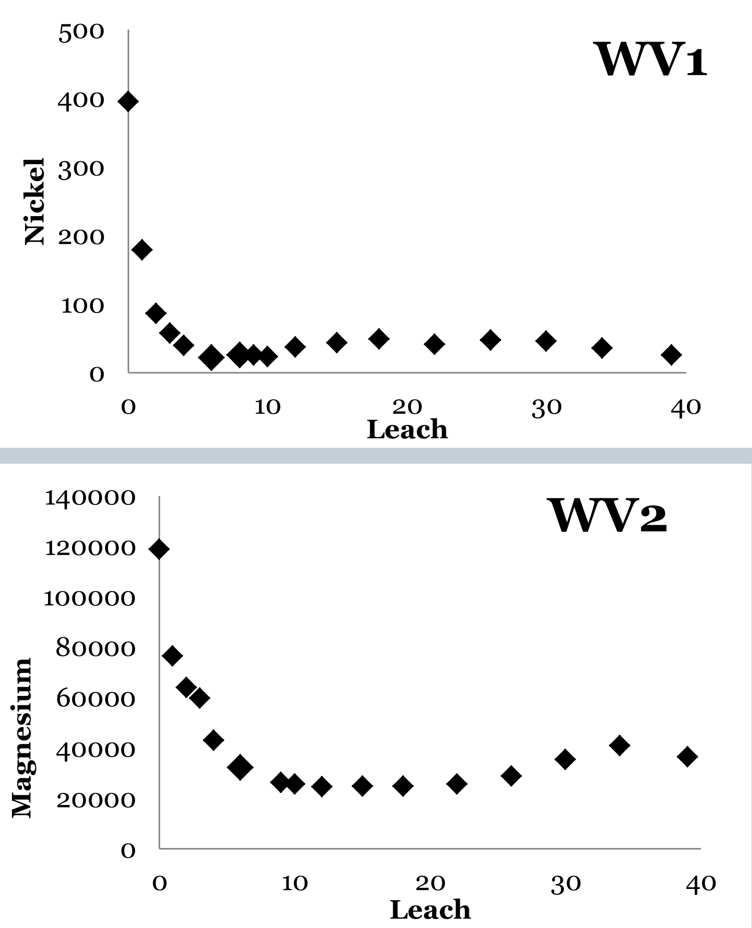
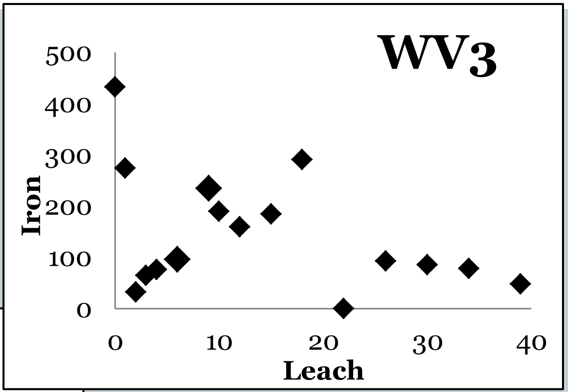
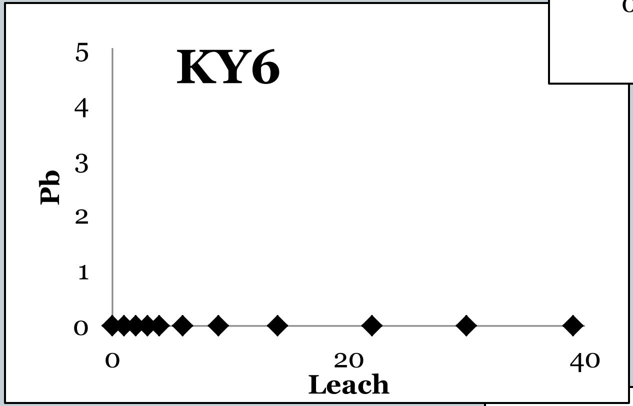


Figure 6. Example "Type 1" (top) and "Type 2" (bottom) leaching patterns.

Leaching Behavior Classification (Cont.)

3. Random or no apparent trend
   - Uncommon-but mostly minor ions
4. All very low with no change (close to detection limit) OR none detected in any leach
   - Cd and Pb
5. Bell-shaped
   - Only for VA 9 (Al and Fe) and KY 11 (Al)





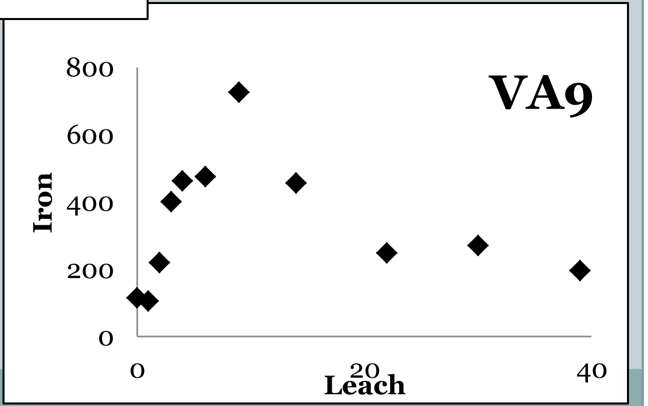


Figure 7. Example "Type 3" (top), "Type 4" (middle), and "Type 5" (bottom) leaching patterns.

Bicarbonate Variability

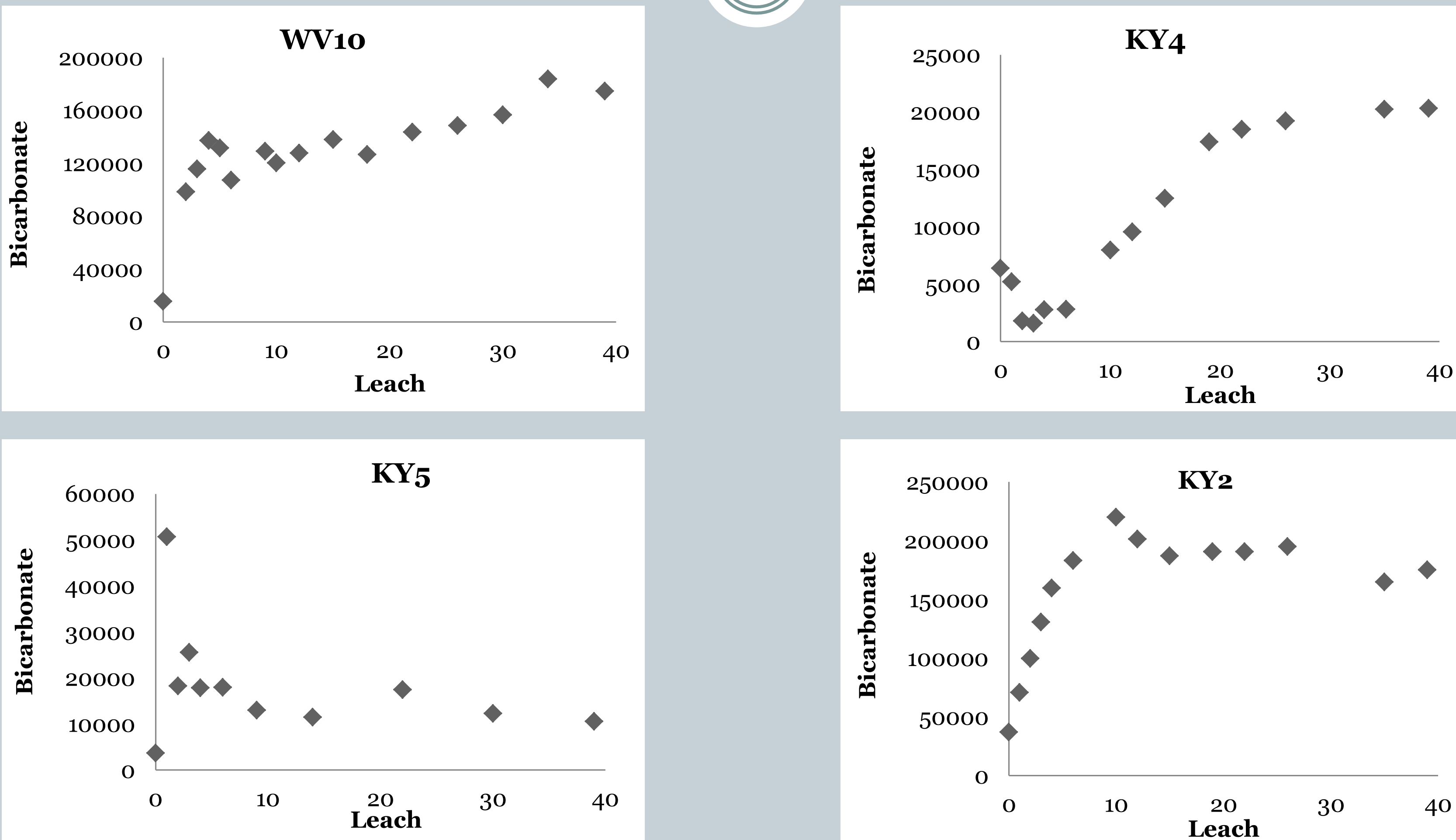
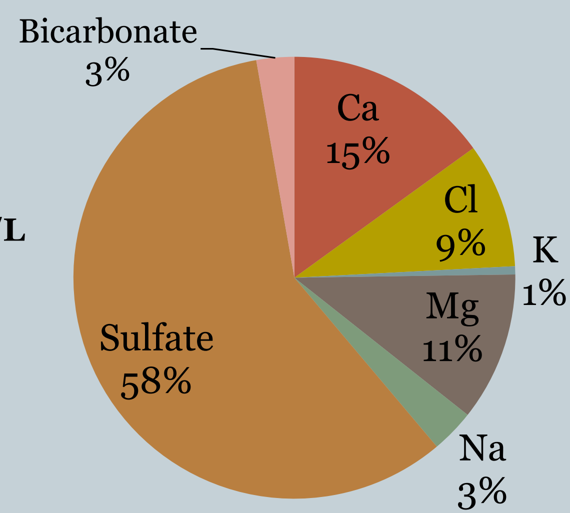


Figure 8. Example bicarbonate leaching patterns the variability of leaching behavior for different mine spoil samples.

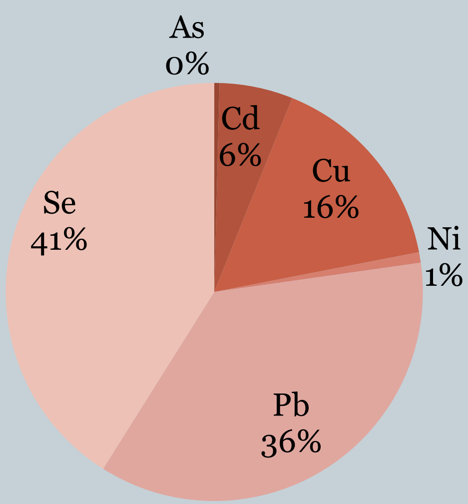
Sandstone Ion Proportions

PEAK

TDS=1240 mg/L

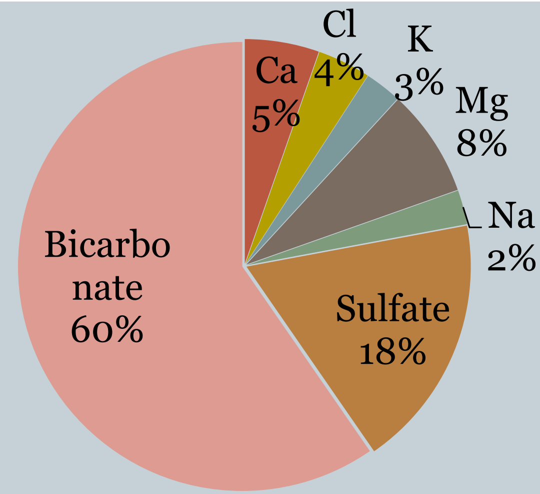


Sum (Minors)= 8027 µg/L

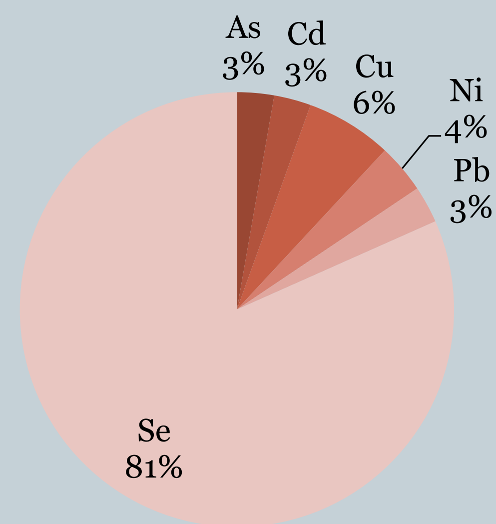


TAIL

TDS=40 mg/L



Sum (Minors)= 1257 µg/L



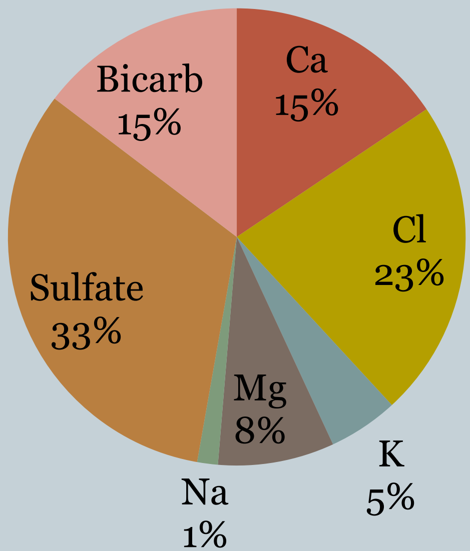
KY 1: Weathered Sandstone

Mudstone and Mixed Rock Ion Proportions

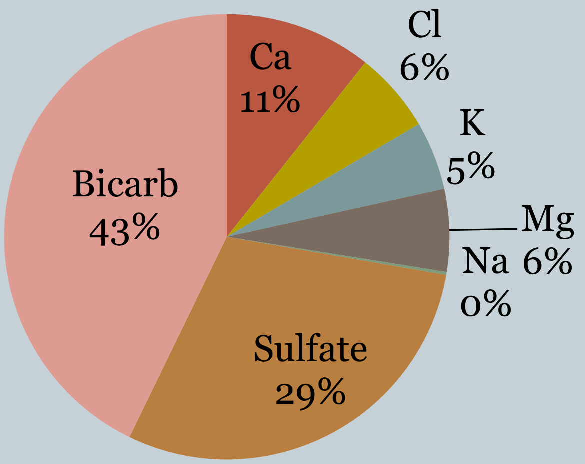
PEAK

TAIL

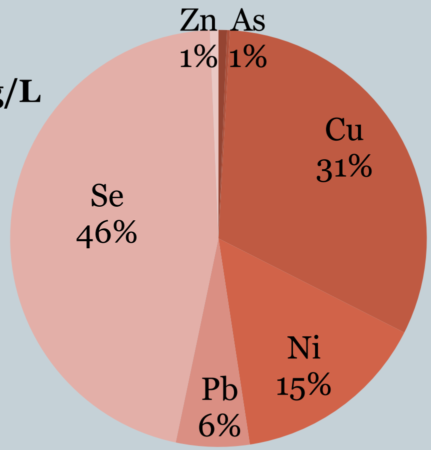
TDS= 836.6 mg/L



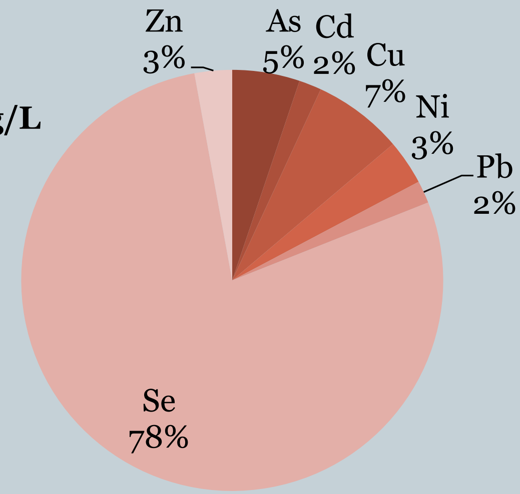
TDS= 254.2 mg/L



Sum (Minors)= 5893 µg/L



Sum (Minors)= 351 µg/L



WV7 : Unweathered Mixed Spoil

Mineralogical Assemblages

- Framework Grains (64-96%)
  - Quartz, Feldspars, Lithic Fragments (metamorphic and sedimentary), Muscovite, Biotite
- Cement/Non-framework (0-23%)
  - Pyrite, Silica cement, Kaolinite cement, Carbonate
- Dissolution (0-10%)
- Replacements (2-21%)
  - Altered feldspars, Goethite, Siderite

Figure 9. Example thin section of a lithic sandstone.

http://facstaff.gpc.edu/~pgore/Levin9e/chaptertutorials/images/fig_05_24.jpg

Mineral Photomicrographs

Show the complex mineralogical compositions of the collected mine spoils

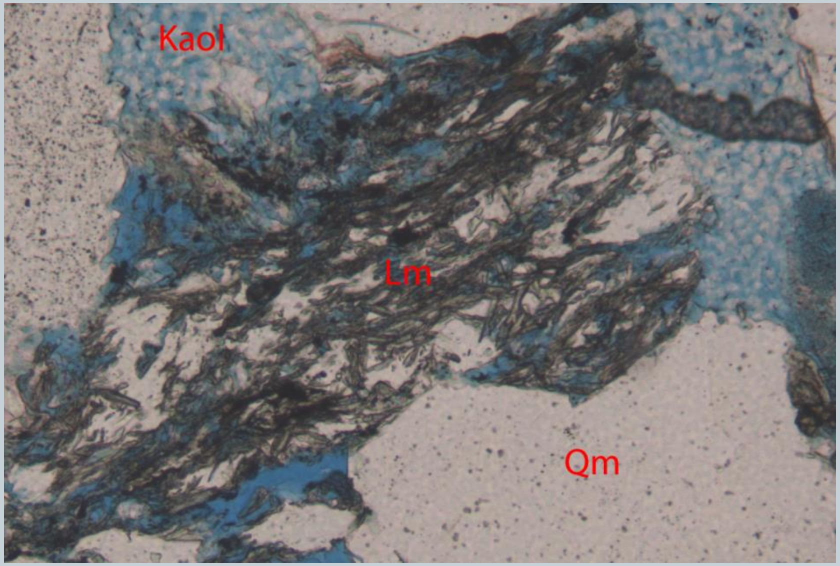


Figure 10. Photomicrograph of the WV10 sample showing a mineralogical composition of quartz (Qm), kaolinite (Kaol) and metamorphic lithic fragments (Lm).

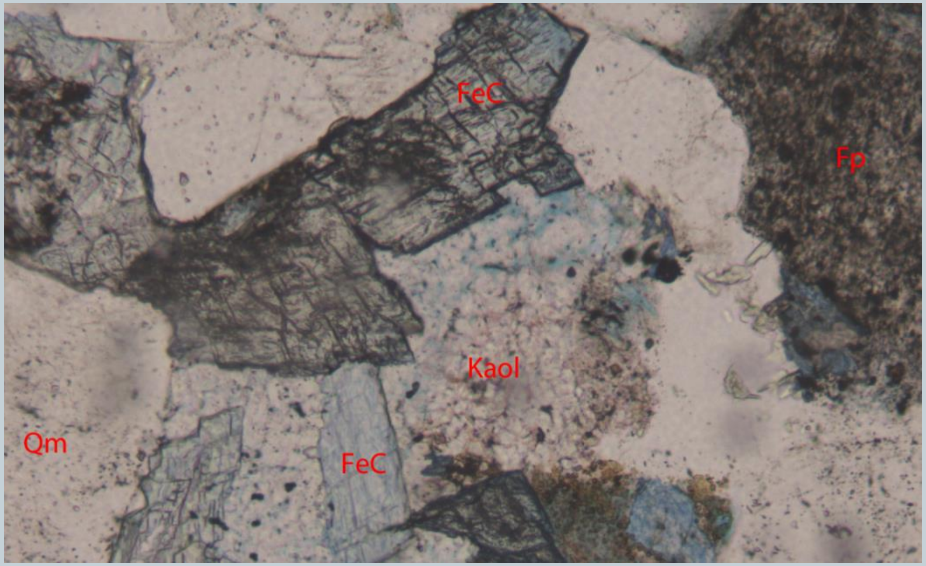
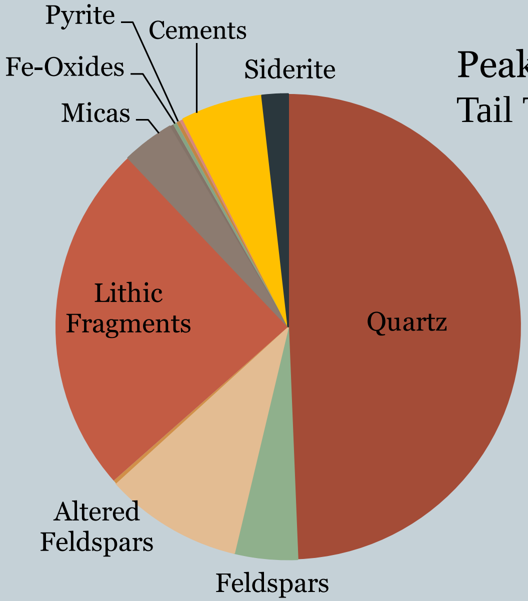


Figure 11. Photomicrograph of the KY3 sample showing feldspar (Fp), quartz (Qm), kaolinite (Kaol), and siderite (FeC).

Ex: Mineralogical Composition (WV4)

- Quartz and lithic fragments are dominant
  - Quartz can range from 25-50% and lithics from 2-45%
- Feldspar alteration to kaolinite is very common
- Goethite very high for some samples
  - Indicators of weathering



Peak TDS: 690 µS/cm
Tail TDS: 352 µS/cm

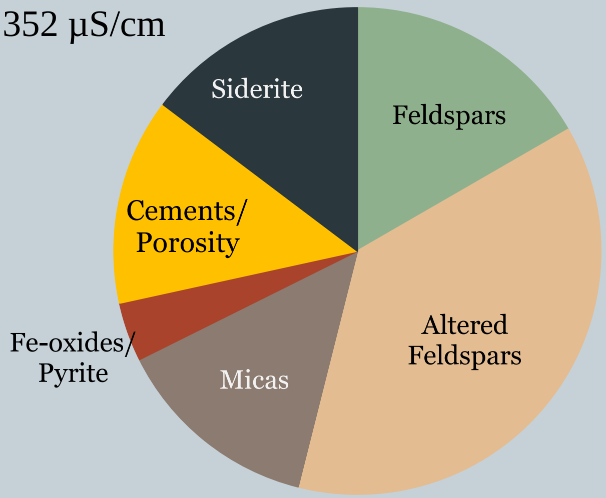


Figure 12. Mineralogical composition of the WV4 spoil sample with quartz and lithic fragments included (left) and excluded (right).

WV4: Unweathered Sandstone

Mineralogical Compositions

Table 1. Identified minerals in mine spoils and associated ionic compositions*.

		K	Na	Ca	Mg	Fe	Mn	Ni	Al	Si	OH	S	CO_3
Framework Grains	Quartz									✓			
	Feldspars	✓	✓	✓		✓			✓	✓			
	Metam. Lithics	✓			✓	✓			✓	✓	✓		
	Sed. Lithics					✓							✓
	Muscovite	✓							✓	✓	✓		
	Biotite	✓			✓	✓			✓	✓	✓		
Other	Chlorite				✓	✓	✓	✓	✓	✓	✓		
	Goethite					✓					✓		
	Pyrite					✓						✓	
	Siderite					✓							✓
	Carbonates			✓	✓	✓							✓

*collected from literature, not measured directly

Average Feldspar Elemental Composition

- Silica is the largest component in feldspars

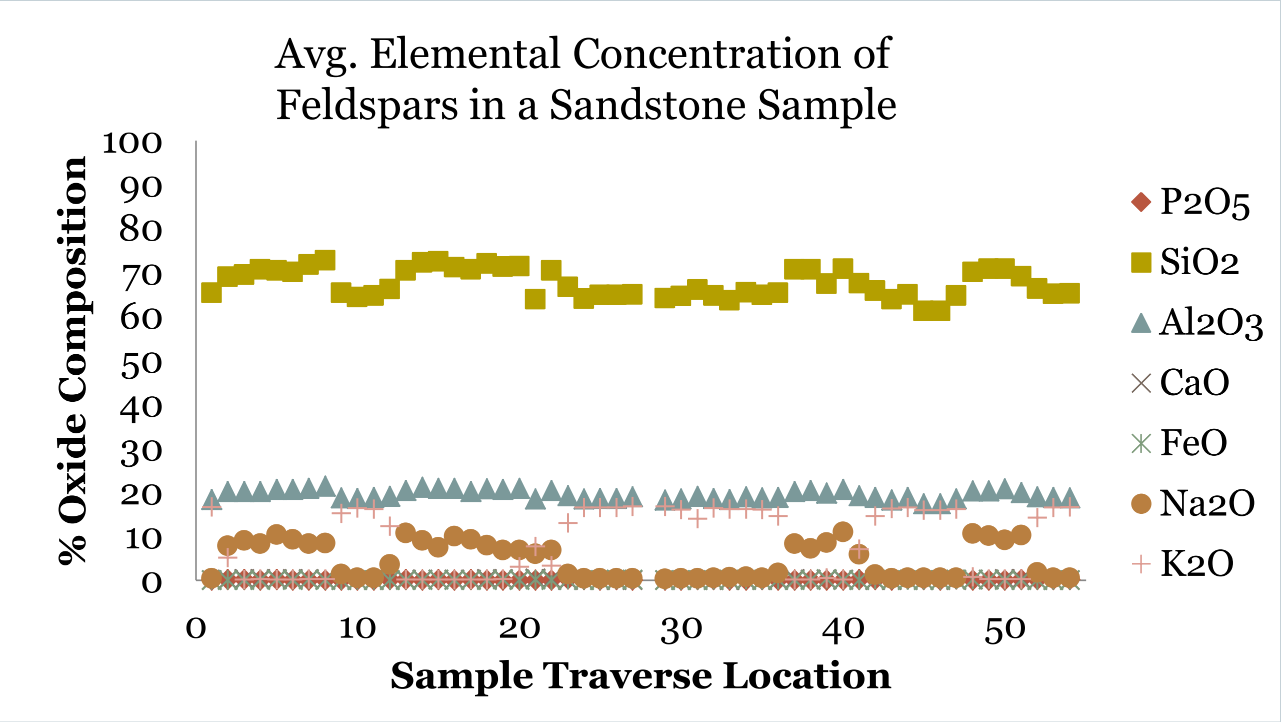


Figure 13. Silica has the largest composition (%) in feldspars .

Feldspar Composition (Continued)

- Feldspar grains contain multiple K and Na-rich zones
- Feldspars do not appear to be a major source of Fe or P

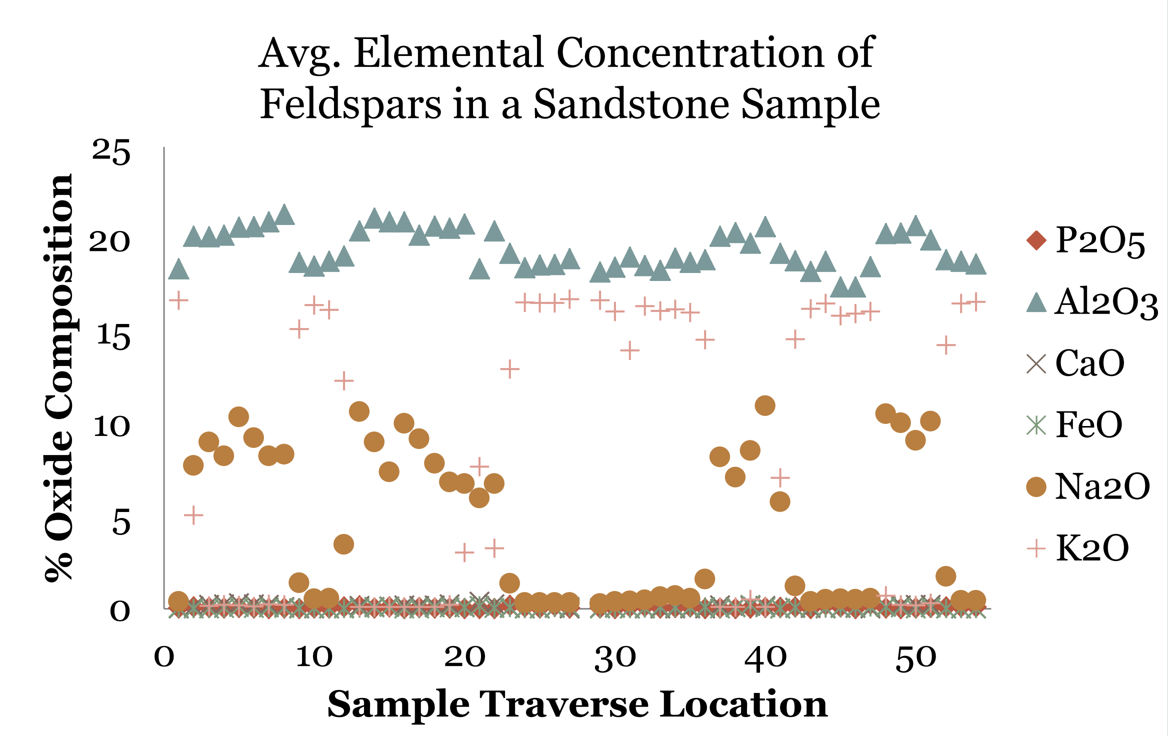


Figure 14. Feldspars contain regions of Al, K and Na-rich zones.

Mineralogical Observations

- VA5 and KY3:
  - Largest EC (TDS) concentrations (2500-2800 µS/cm)
  - Largest sulfate and Mg concentration, high Ca
  - Largest counts of “reactive” minerals: carbonate, siderite, pyrite, Fe-oxides
  - Large feldspar counts and feldspar alteration to kaolinite
  - Low in lithic fragments

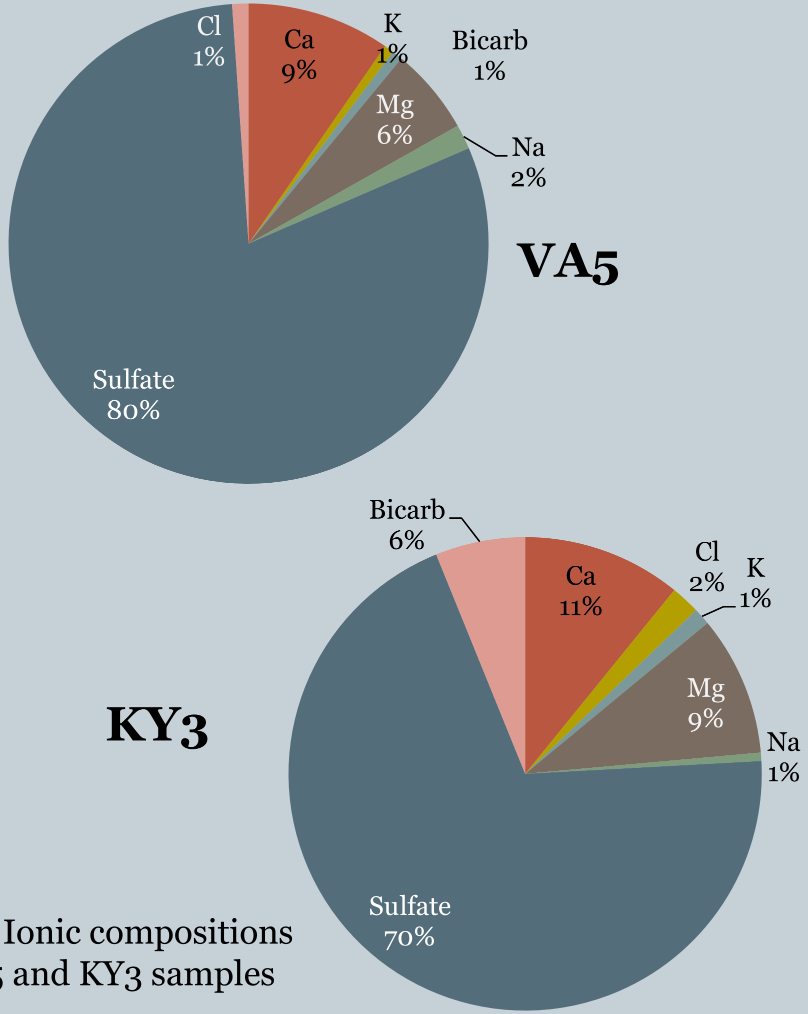


Figure 15. Ionic compositions of the VA5 and KY3 samples at Leach 0.

Conclusions

- Spoil leaching behavior is complex:
  - There are different patterns of ion release; bicarbonate behaves differently than all other ions
  - Analyses to date show no patterns in minor ion chemistry based on rock type, weathering type or mineralogy
- Mineralogy aids in identifying ion sources:
  - Feldspars have multiple Na and K-rich zones within grains
  - Feldspar alteration to kaolinite is very common
  - Lithic fragment counts range widely and indicate spoil complexity
  - "Reactive" minerals (carbonate, siderite, pyrite, goethite) are likely driving TDS release

Acknowledgements

- Direct financial support by OSM Applied Research Program-Pittsburgh, Powell River Project, Virginia Tech Institute for Critical Technology and Applied Sciences (ICTAS), and ARIES (see next slide).
- Cooperative work with Jeff Skousen and Louis McDonald at WVU and Carmen Agouridis, Chris Barton, and Richard Warner at UK.

ARIES Statement

A portion of the work reported today was sponsored by the Appalachian Research Initiative for Environmental Science (ARIES). ARIES is an industrial affiliates program at Virginia Tech, supported by members that include companies in the energy sector. The research under ARIES is conducted by independent researchers in accordance with the policies on scientific integrity of their institutions. The views, opinions and recommendations expressed herein are solely those of the authors and do not imply any endorsement by ARIES employees, other ARIES-affiliated researchers or industrial members. Information about ARIES can be found at http://www.energy.vt.edu/ARIES

Questions?