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Abstract: A rapid batch extraction method was evaluated to estimate potential for total dissolved solids (TDS) release by 65 samples of rock from coal and gas-bearing strata of the Appalachian Basin in eastern USA. Three different extractant solutions were considered: deionized water (DI), DI equilibrated with 10% CO2 atmosphere (DI+CO2), or 30% H2O2 under 10% CO2 (H2O2+CO2). In all extractions, 10 g of pulverized rock (<0.5-mm) were mixed with 20 mL of extractant solution and shaken for 4 hours at 50 rpm and 20-22oC. The 65 rock samples were classified as coal (n=3), overburden (n=17), coal refuse that had weathered in the field (n=14), unleached coal refuse that had oxidized during indoor storage (n=20), gas-bearing shale (n=10), and pyrite (n=1). Extracts were analyzed for specific conductance (SC), TDS, pH, and major and trace elements, and subsequently speciated to determine ionic contributions to SC. The pH of extractant blanks decreased in the order DI (6.0), DI+CO2 (5.1), and H2O2+CO2 (2.6). The DI extractant was effective for mobilizing soluble SO4 and Cl salts. The DI+CO2 extractant increased weathering of carbonates and resulted in equivalent or greater TDS than the DI leach of same material. The H2O2+CO2 extractant increased weathering of sulfides (and carbonates) and resulted in greatest TDS production and lowest pH values. Of the 65 samples, 19 had leachate chemistry data from previous column experiments and 35 were paired to 10 field sites with leachate chemistry data. When accounting for the water-to-rock ratio, TDS from DI and DI+CO2 extractions were correlated to TDS from column experiments while TDS from H2O2+CO2 extractions was not. In contrast to column experiments, field SC was better correlated to SC measured from H2O2+CO2 extractions versus DI extractions. The field SC and SC from H2O2+CO2 extractions were statistically indistinguishable for 7 of 9 paired data sets while SC from DI extractions underestimated field SC in 5 of 9 cases. Upscaling comparisons suggest that (1) weathering reactions in the field are more aggressive than DI water or synthetic rainwater extractants used in batch or column tests, and (2) a batch extraction method utilizing 30% H2O2 (which is mildly acidic without CO2 enrichment)

could be effective for identifying rocks that will release high amounts of TDS.

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Research Data Related to this Submission

Title: Data for: Batch Extraction Method to Estimate Total Dissolved Solids (TDS) Release from Coal Refuse and Overburden
Repository: Mendeley Data
https://data.mendeley.com/datasets/h3dthbdv99/draft?a=28425219-bd6a-460b-97c1-d723fb361294

Cover Letter

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July 2, 2019

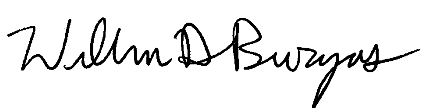
Dear Editor,

We are pleased to submit the manuscript "Batch Extraction Method to Estimate Total Dissolved Solids (TDS) Release from Coal Refuse and Overburden" by Luis Castillo Meza, Charles Cravotta, Travis Tasker, Nat Warner, Lee Daniels, Zenah Orndorf, Tim Bergstresser, May Douglass, George Kimble, Joelle Streczywilk, Chris Barton, Stephanie Fulton, Aaron Thompson, and myself to *Applied Geochemistry*. I am the corresponding author and all my contact information is included below. Through the online submission portal, we input contact information for five suggested reviewers.

Our manuscript demonstrates that a relatively simple and rapid batch extraction test can be used to estimate the mass of TDS released from freshly unearthed rock. These results are significant and highly applied because they provide a tool to manage water quality impacts associated with any earth-moving operation (e.g., surface mining, highway construction, land development). This manuscript presents the most comprehensive data set that we are aware of that combines batch extraction data for 65 samples of rock from coal and gas-bearing strata of the Appalachian Basin in the eastern United States (all newly reported), with data from 'up-scaled' results from column leaching experiments (most previously reported) and from field monitoring stations (most newly reported). We demonstrate that a batch extraction method utilizing 30% H_2O_2 (which is mildly acidic) could be effective for identifying rocks that will release high amounts of TDS.

We strongly believe this work would be of great interest to the readers of *Applied Geochemistry*.

Sincerely,



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Batch Extraction Method to Estimate Total Dissolved Solids (TDS) Release from Coal Refuse and Overburden

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Abstract

A rapid batch extraction method was evaluated to estimate potential for total dissolved solids (TDS) release by 65 samples of rock from coal and gas-bearing strata of the Appalachian Basin in eastern USA. Three different extractant solutions were considered: deionized water (DI), DI equilibrated with 10% CO_2 atmosphere (DI+CO_2), or 30% H_2O_2 under 10% CO_2 (H_2O_2+CO_2). In all extractions, 10 g of pulverized rock (<0.5-mm) were mixed with 20 mL of extractant solution and shaken for 4 hours at 50 rpm and 20-22°C. The 65 rock samples were classified as coal (n=3), overburden (n=17), coal refuse that had weathered in the field (n=14), unleached coal refuse that had oxidized during indoor storage (n=20), gas-bearing shale (n=10), and pyrite (n=1). Extracts were analyzed for specific conductance (SC), TDS, pH, and major and trace elements, and subsequently speciated to determine ionic contributions to SC. The pH of extractant blanks decreased in the order DI (6.0), DI+CO_2 (5.1), and H_2O_2+CO_2 (2.6). The DI extractant was effective for mobilizing soluble SO_4 and Cl salts. The DI+CO_2 extractant increased weathering of carbonates and resulted in equivalent or greater TDS than the DI leach of same material. The H_2O_2+CO_2 extractant increased weathering of sulfides (and carbonates) and resulted in greatest TDS production and lowest pH values. Of the 65 samples, 19 had leachate chemistry data from previous column experiments and 35 were paired to 10 field sites with leachate chemistry data. When accounting for the water-to-rock ratio, TDS from DI and DI+CO_2 extractions were correlated to TDS from column experiments while TDS from H_2O_2+CO_2 extractions was not. In contrast to column experiments, field SC was better correlated to SC measured from H_2O_2+CO_2 extractions versus DI extractions. The field SC and SC from H_2O_2+CO_2 extractions were statistically indistinguishable for 7 of 9 paired data sets while SC from DI extractions underestimated field SC in 5 of 9 cases. Upscaling comparisons suggest that (1) weathering reactions in the field are more aggressive than DI water or synthetic rainwater extractants used in batch or column tests, and (2) a batch extraction method utilizing 30% H_2O_2 (which is mildly acidic without CO_2 enrichment) could be effective for identifying rocks that will release high amounts of TDS.

1. Introduction

High salinity in streams downgradient of coal-mining and processing facilities in the eastern U.S. has caused fish kills and harmed sensitive aquatic organisms within the past decade (Barrett, 2015; Cormier et al., 2013a; Cormier et al., 2013b; Pond et al., 2008). At the same time, higher than normal concentrations of total dissolved solids (TDS), chloride, and bromide have been documented in the Allegheny and Monongahela Rivers in western Pennsylvania (Wang, 2014; Ziemkiewicz, 2015a), while a gradual increase in salinity attributed to chloride has been documented in major rivers in the northeastern U.S. (Kaushal et al., 2005, 2018). Such observations for coal-mine drainage in the northern Appalachian Basin may be explained by recent changes in resource extraction activities that can be influenced by residual brine in the rock, including the underground mining of coal into progressively deeper zones, the development of coal-bed methane, and the development of shale gas reserves in strata below the coal-bearing formations, notably the Marcellus Shale (Cravotta and Brady, 2015; Donovan and Leavitt, 2004; Donovan et al., 2015; Ziemkiewicz, 2015a). An understanding of the potential sources of salinity at local and watershed scales is necessary for the development of effective strategies to minimize and mitigate aquatic impacts from elevated TDS.

Accelerated mineral weathering generally accounts for increased TDS release from coal-mining landscapes (Brady et al., 1998; Timpano et al., 2010, 2015). Although acidic drainage and TDS release are commonly attributed to abandoned mines, the use of overburden materials as topsoil substitutes and the placement of carbonate-bearing overburden materials can contribute to elevated TDS (Bernhardt et al., 2012; Cormier et al., 2013; Zipper et al., 2015). Topsoil substitution with overburden is explicitly allowed in the Surface Mining Control and Reclamation Act (SMCRA), and the application of acid-base accounting (ABA) procedures guides placement of alkaline strata with the explicit goal of decreasing acidity from sulfide oxidation (Skousen et al., 2002). Oxidative dissolution of sulfide minerals will release dilute sulfuric acid, iron, and other metal(loids). Subsequent neutralization of sulfuric acid by carbonate minerals, used in ABA to balance acid generation, results in the release of calcium, magnesium, and bicarbonate. Although silicate mineral weathering rates are slower than those of carbonates, silicates predominate in coal overburden and can be significant sources of calcium, magnesium, sodium, potassium, aluminum, and silicon (Brady et al., 1998; Clark et al., 2018; Hammarstrom et al., 2009). Dissolution of salts or *in situ* brines retained in the rock also releases sodium, calcium, sulfate, and chloride (as well as, barium, strontium, and bromide).

Laboratory-scale column and mesocosm-scale lysimeter experiments have been used to predict TDS release from coal industry materials (overburden, refuse, combustion byproducts) for nearly three decades (e.g., Brady et al., 1998; Clark et al., 2018; Daniels et al., 2014a; Daniels et al., 2016; Daniels et al., 2014b; Hornberger et al., 2004; Orndorff et al., 2015). These studies have shown that (1) rock type and extent of weathering influence TDS release, (2) shales and mudstones release more TDS than sandstones, and (3) unweathered rocks release more TDS than weathered materials. The specific conductance (SC) of column leachates typically starts near peak values, decreases during the first few pore volume leach cycles, and then stabilizes over the remaining leach cycles. For weathered overburden materials, peak leachate SC was often less than 500 $\mu S\ cm^{-1}$, a proposed regulatory limit (Cormier et al., 2013). Coal refuse produced during coal processing generated considerably higher peak SC and associated concentrations of TDS, acidity, and major and trace elements compared to overburden and interburden strata removed during mining operations (Cravotta and Brady, 2015; Daniels et al., 2014b; Orndorff et al., 2015). In one study (Daniels et al., 2014b), columns (0.0012 m^3 rock) were upscaled to mesocosms (1.5 m^3 rock) using the same rock samples but with larger size fragments than in the columns. SC declined significantly in both the columns and the mesocosms. Compared to the columns, the peak leachate SC was higher and the temporal decline of SC was not as steady in the mesocosms likely because the mesocosms were in operated in a less controlled environment. In either case, the use of such laboratory and field kinetic tests can involve months to years to obtain results and generally requires kg of rock materials.

A rapid batch extraction method that can be used to test small quantities of representative materials and that correlates well with field leachates would be of value to identify and manage rock types that release high TDS, and to characterize TDS from different energy extraction activities. For in-field determinations, “rapid” could refer to days if samples were shipped to a commercial laboratory, or hours if rock samples could be crushed and sieved, reacted with extractant solutions, and quantified for TDS release based on SC using a portable meter (discussed below). Because ABA parameters such as maximum potential acidity (MPA) and net neutralization potential (NNP) are used by coal companies to characterize overburden and are readily measured, their ability to predict TDS release has been evaluated. Odenheimer et al. (2014) demonstrated that MPA and NNP may be useful to indicate general levels of low, moderate, and high TDS release; however, their semi-quantitative model was based on TDS computed from paste SC for a pulverized rock sample and did not consider upscaled or field-measured leachate characteristics. Modifying a method described by Barnhisel and Harrison (1976) and O’Shay et al. (1990), Orndorff et al. (2010) developed an alternative to the MPA method that used hydrogen peroxide (30% H_2O_2) to oxidize sulfide minerals. They found that the peroxide potential acidity (PPA) was better than MPA as a predictor of TDS release from low-S rocks. However, the potential application of PPA to predict TDS release from a wide range of rock types was not evaluated.

The objectives of this research were to 1) develop and test a batch extraction method to predict TDS release from a range of rock types associated with energy extraction, 2) compare different batch extraction methods to results reported for column leaching tests and field-scale leachate, 3) evaluate those batch extraction methods to determine the most reliable method to quantify TDS release, and 4) identify tracers in leachate that may distinguish coal mining-derived TDS from other energy extraction sources.

2. Materials and Methods

2.1 Sample Collection and Preparation

A total of 65 sedimentary rock and coal samples were obtained from multiple sources (Table 1). The samples represent important fossil fuel-bearing strata in the Appalachian Basin, including bituminous coals and gas-producing shales. Eleven rock samples (3 weathered coal refuse, 8 overburden) were provided by Virginia Tech. Equivalent samples had been previously used in laboratory-scale, flow-through unsaturated column leaching experiments (Daniels et al., 2016; Daniels et al., 2014b; Orndorff et al., 2015). Six rock samples (5 overburden, 1 pyrite) were provided by the U.S. Geological Survey

Table 1. Descriptions of the 65 rock samples tested.

ID	Source[1]	Operational Rock Type[2]	Lithology	WE[3]	Geologic Unit	Stratigraphic Formation	Mineralogy[4]	Data for Upscaling[5]
PA1	Mine A	Coal	Coal	W	L. Kittanning	Kittanning	Qtz, Cal, Kln, Py, Ms	n.a.
PA5	Mine A	Coal	Coal	W	L. Kittanning	Kittanning	Qtz, Kln, Py, Ms	--
PA45	Mine B	Coal	Coal	W	L. Kittanning/ U. Kittanning/ Freeport	Kittanning and Allegheny	Qtz, Kln, Jr, Ms	n.a.
PA12	Mine A	W. Refuse	Coal and shale	W	L. Kittanning	Kittanning	Qtz, Gp, Kln, Ms, Jr,	FL
PA13	Mine A	W. Refuse	Coal and shale	W	L. Kittanning	Kittanning	Qtz, Gp, Kln, Ms, Jr,	FL
PA17	Mine A	W. Refuse	Coal and shale	W	L. Kittanning	Kittanning	Qtz, Kln, Ms, Py,	FL
PA22	Mine A	W. Refuse	Coal and shale	W	L. Kittanning	Kittanning	Qtz, Ms, Kln, Py, Gp, Vrm	FL
PA30	Mine A	W. Refuse	Coal and shale	W	L. Kittanning	Kittanning	Qtz, Cal, Kln, Py, Ms, Gp	FL
PA31	Mine B	W. Refuse	Coal and shale	W	L. Kittanning/ U. Kittanning/ Freeport	Kittanning and Allegheny	Qtz, Gp, Ms, Kln, Py, Cal, Vrm	FL
PA36	Mine B	W. Refuse	Coal and shale	W	L. Kittanning/ U. Kittanning/ Freeport	Kittanning and Allegheny	Qtz, Kln, Ms, Py, Vrm	FL
PA42	Mine B	W. Refuse	Coal and shale	W	L. Kittanning/ U. Kittanning/ Freeport	Kittanning and Allegheny	Qtz, Klm, Ms, Gp, Vrm	FL
PA48	Mine B	W. Refuse	Coal and shale	W	L. Kittanning/ U. Kittanning/ Freeport	Kittanning and Allegheny	Qtz, Ms, Kln, Gp, Py, Vrm	FL
PA51	Mine B	W. Refuse	Coal and shale	W	L. Kittanning/ U. Kittanning/ Freeport	Kittanning and Allegheny	Qtz, Ms, Kln, Gp, Vrm	FL
PA58	Mine B	W. Refuse	Coal and shale	W	L. Kittanning/ U. Kittanning/ Freeport	Kittanning and Allegheny	Qtz, Ms, Kln, Gp, Jr, Vrm	FL
TNR1	VT	W. Refuse	n.a. [6]	n.a.	Graves Gap refuse	Graves Gap	Qtz, Ms, Kln, Vrm	CL
TNR2	VT	W. Refuse	n.a.	n.a.	Graves Gap refuse	Graves Gap	Qtz, Cal, Ms, Kln, Gp, Vrm	CL
TNR3	VT	W. Refuse	n.a.	n.a.	Graves Gap refuse	Graves Gap	Qtz, Ms, Kln, Vrm, Py	CL
TGS1	PA	U. Refuse	Coal and shale	U	Pittsburgh	Monongahela	Qtz, Py, Kln, Ms, Vrm	FL
TGS2A	PA	U. Refuse	Coal and shale	U	Pittsburgh	Monongahela	Qtz, Poi, Py, Kln	--
TGS2B	PA	U. Refuse	Coal and shale	U	Pittsburgh	Monongahela	Qtz, Kln, Ms	FL
TGS3	PA	U. Refuse	Claystone	U	Pittsburgh	Monongahela	Qtz, Cal, Kln, Ms, Py	FL
TGS4	PA	U. Refuse	Shale	U	Pittsburgh	Monongahela	Qtz, Kln, Ms, Vrm	--
TGS5	PA	U. Refuse	Coal and shale	U	Pittsburgh	Monongahela	Qtz, Poi, Py, Kln	FL
TGS6	PA	U. Refuse	Shale	U	Pittsburgh	Monongahela	Qtz, Kln, Ms	FL
TGS7A	PA	U. Refuse	Claystone	U	Pittsburgh	Monongahela	Qtz, Cal, Ms, Kln	FL
TGS7B	PA	U. Refuse	Claystone	U	Pittsburgh	Monongahela	Qtz, Kln, Py , Ms	FL
TGS8	PA	U. Refuse	Coal and shale	U	Pittsburgh	Monongahela	Qtz, Kln, Ms ,Poi, Rz	FL
TGS9	PA	U. Refuse	Shale	U	Pittsburgh	Monongahela	Qtz, Kln, Ms	FL
TGS10A	PA	U. Refuse	Coal and shale	U	Pittsburgh	Monongahela	Qtz, Rz, Kln, Py, Ms	--
TGS10B	PA	U. Refuse	Coal and shale	U	Pittsburgh	Monongahela	Qtz, Kln, Ms, Rz	FL
TGS11	PA	U. Refuse	Shale	U	Pittsburgh	Monongahela	Qtz, Kln, Ms	FL
TGS12	PA	U. Refuse	Shale	U	Pittsburgh	Monongahela	Qtz, Gp, Py, Kln, Ms	FL
TGS13	PA	U. Refuse	Shale	U	Pittsburgh	Monongahela	Cal, Qtz, Kln	FL

Table 1. Descriptions of the 65 rock samples tested (continued).

ID	SM[1]	Operational Rock Type[2]	Lithology	WE[3]	Geologic Unit	Stratigraphic Formation	Mineralogy[4]	Data for Upscaling[5]
TGS14	PA	U. Refuse	Coal and shale	U	Pittsburgh	Monongahela	Qtz, Ms, Klm, Py, Vrm	FL
TGS15	PA	U. Refuse	Claystone	U	Pittsburgh	Monongahela	Qtz, Klm, Ms, Py	FL
TGS16	PA	U. Refuse	Claystone	U	Pittsburgh	Monongahela	Qtz, Py , Klm, Ms	FL
TGS17	PA	U. Refuse	Claystone	U	Pittsburgh	Monongahela	Qtz, Klm , Ms, Cal, Py	FL
BCS3	USGS	Overburden	Shale	U	Brush Creek shale	Glenshaw	Qtz, Ms, Kln, Chl, Vrm, Cal, Py	CL, FL
HCS	USGS	Overburden	Shale	U	Houchin Creek shale	Carbondale	Qtz, Gp, Ms, Ill, Chl, Kln, Jr, Py, Ab, Vrm	CL
KBFWV	USGS	Overburden	Shale	U	Black Flint shale	Kanawha	Qtz, Kln, Ms, Dol, Sd, Ab, Vrm	CL
LKFC	USGS	Overburden	Shale	U	L. Kittanning	Kittanning	Qtz, Ms, Chl, Ill, Kln, Vrm, Gp, Py, Sd	CL, FL
MKSS	USGS	Overburden	Sandstone	U	M. Kittanning	Kittanning	Qtz, Ms, Kln, Chl, Vrm, Gp, Cal, Sd	CL
KY1	UK	Overburden	Sandstone	W	Princess	Princess	Qtz, Kln, Vrm, Dol, Sd, Gt	CL, FLY
KY2	UK	Overburden	Sandstone	U	Four Corners	Four Corners	Qtz, Kln, Vrm, Dol, Sd	CL, FLY
KY3	UK	Overburden	Mixed	W	Four Corners	Four Corners	Qtz, Kln, Vrm, Dol, Sd, Gt	CL, FLY
KY4	UK	Overburden	Mixed?	U	Four Corners	Four Corners	Qtz, Kln, Vrm	CL
KY7	VT	Overburden	Mixed	U	Four Corners black shale	Four Corners	Qtz, Ms, Kln, Ab, Gp, Vrm	CL, FL
KY9	VT	Overburden	Mixed	U	Four Corners mixed	Four Corners	Qtz, Ms, Kln, Vrm	CL
TN2	VT	Overburden	Shale mix	n.a.	Windrock, Lower Dean, Dean	Anderson and Glen Dean	n.a.	CL
VA2	VT	Overburden	Black shale	U	Four Corners black shale	Four Corners	Qtz, Ms, Kln, Vrm	CL
VA3	VT	Overburden	Mixed	U	M. Wise mixed	Wise	Qtz, Ms, Kln, Ab, Vrm	CL
VA6	VT	Overburden	Mudstone	U	Lower Wise mudstones	Wise	Qtz, Ms, Kln, Vrm	--
VA16	VT	Overburden	Sandstone	U	Harlan Sandstone	Harlan	Qtz, Ms, Kln, Vrm	CL
WV5	VT	Overburden	Sandstone	U	Kanawha Sandstone	Kanawha	Qtz, Ms, Kln, Vrm	CL
SHJ1	NDA	Shale	Shale gas	U	Utica Shale	Utica	Qtz, Cal, Ms, Kln, Dol, Py, Vrm	--
SHJ2	NDA	Shale	Shale gas	U	Utica Shale	Utica	Qtz, Cal, Ms, Kln, Dol, Py, Vrm	--
SHJ3	NDA	Shale	Shale gas	U	Utica Shale	Utica	Qtz, Cal, Ms, Kln, Dol, Py, Vrm	--
SHJ4	NDA	Shale	Shale gas	U	Utica Shale	Utica	Qtz, Cal, Ms, Kln, Dol, Py, Vrm	--
SHJ5	NDA	Shale	Shale gas	U	Utica Shale	Utica	Qtz, Cal, Ms, Kln, Dol, Py, Vrm	--
SHM1	NDA	Shale	Shale gas	U	Utica Shale	Utica	Qtz, Kln, Ms, Dol, Py	--
SHM2	NDA	Shale	Shale gas	U	Utica Shale	Utica	Qtz, Kln, Ms, Dol, Py	--
SHM3	NDA	Shale	Shale gas	U	Utica Shale	Utica	n.a.	--
SHO1	OH	Shale	Shale gas	U	Utica Shale	Utica	Qtz, Cal, Ms, Kln, Vrm, Py, Dol	--
SHE1	PA	Shale	Shale gas	U	Marcellus Shale	Marcellus	Qtz, Cal, Ms, Kln, Vrm, Gp, Py	--
SKYPA	USGS	Pyrite	Pyrite	n.a.	Bald Eagle Sandstone	Bald Eagle	Qtz, Ms, Py	FR

[1] Source: OH = Ohio Geologic Survey; NDA = Penn State Non-disclosure agreement; PA = Pennsylvania Bureau of Topographic and Geologic Survey; USGS = U.S. Geological Survey; UK = University of Kentucky; VT = Virginia Tech.

[2] U. Refuse = Unleached refuse; W. Refuse = Weathered refuse.

[3] WE = Weathering extent: U = Unweathered (partly oxidized while stored indoors but unleached); W = Weathered (partly oxidized and leached outdoors).

[4] Minerals identified by XRD and are listed in semi-quantitative order of abundance. Ab = albite; Cal = calcite; Chl = chlorite; Dol = dolomite; Gp = gypsum; Gt = goethite; Ill = illite; Jr = jarosite; Kln = Kaolinite; Ms = muscovite; Poi = poitevinite; Py = pyrite; Qtz = quartz; Rz = rozenite; Sd = siderite; Vrm = vermiculite.

[5] CL = Column leachate; FL = Field leachate; FLY = Field lysimeter; FR = Field runoff.

[6] n.a. = not available.

(USGS). The five overburden samples had been previously characterized and used in laboratory-scale, flow-through column leaching experiments (Hammarstrom et al., 2009; Hornberger and Brady, 2009). The pyrite sample collected from the Bald Eagle Formation during construction of I-99 at the Skytop roadcut in Centre County, PA, along with paired water chemistry measurements had been previously described (Hammarstrom et al., 2005). Four overburden samples were provided by University of Kentucky. Three of these sample materials had been used in field-scale lysimeter studies (mesocosms) (Agouridis et al., 2012; Sena et al., 2014) and all four had also been used in laboratory-scale, flow-through column leaching experiments (Daniels et al., 2016). Twenty unleached coal refuse samples from the roof and floor of the Pittsburgh Coal Formation were collected from drill core materials stored in a repository maintained by the Pennsylvania Bureau of Topographic and Geologic Survey (TopoGeo; Harrisburg, PA). Samples were collected from cores 8009, 8011, 8012, and 8013 that were drilled in Greene County, PA. One unleached Marcellus Shale sample was collected from drill core materials (Sullivan core at 8276 feet) stored by TopoGeo. One unleached Utica/Point Pleasant Shale sample was collected from drill core materials stored in a repository maintained by the Ohio Geologic Survey (Columbus, OH). Eight samples of Utica/Point Pleasant Shale drill cuttings were provided by two gas development companies working in Pennsylvania. Finally, in March 2017, a total of 11 weathered coal refuse samples, 3 coal samples, and 4 coal refuse leachate samples were collected from two coal refuse disposal facilities (referred to as Mine A and Mine B) in western Pennsylvania.

2.2 Rock Type Categorization

Rock samples were sorted into six operational categories: coal (n=3), overburden (n=17), weathered coal refuse (n=14), unleached but oxidized coal refuse (n=20), gas-bearing shale (n=10), and pyrite (n=1) (Table 1). Coal refuse and overburden categories were differentiated based on the definitions in Pennsylvania Code Title 25 (Environmental protection), Chapter 87 (Surface mining coal), Section 87.1 (Definitions) (25 Pa. Code § 87.1) (Commonwealth of Pennsylvania, 2018a). Specifically, overburden is defined as “the strata or material overlying a coal deposit or between coal deposits in its natural state and shall mean material before or after its removal by surface mining”. Coal refuse is defined as "any waste coal, rock, shale, slurry, culm, gob, boney, slate, clay and related materials, associated with or near a coal seam, which are either brought aboveground or otherwise removed from a coal mine in the process of mining coal or which are separated from coal during the cleaning or preparation operations". Shales closer in age and stratigraphic position to coal formations were included in coal refuse or overburden categories. The gas-bearing shale category included only the Utica/Point Pleasant Shale or Marcellus Shale samples. Pyrite included one sample from the Bald Eagle Formation at Skytop roadcut (Hammarstrom et al., 2005).

2.3 Operational Extractions

Once received, rock samples were freeze-dried using a Labconco FreeZone 4.5 freeze dry system until constant weight was attained. Samples were crushed to < 4.75-mm using a hydraulic press at 44.5 kN and thereafter with a mortar and pestle until all particles were < 2-mm in diameter. Samples were then pulverized using a Spex 8000 ball mill to produce particles < 0.5-mm diameter (passed through No. 35 sieve).

Pulverized rock samples were sent to Geochemical Testing, a certified commercial laboratory in Somerset, PA, to conduct three operational extractions and analyze the SC, pH, and solute concentrations of various leachates. A fourth extraction was conducted at Pennsylvania State University to measure strontium isotopes ($^{87}Sr/^{86}Sr$). In Leach 1 (L1), rock samples were reacted with distilled deionized water (DI) under an ambient atmosphere. In Leach 2 (L2), rock samples were reacted with DI water under a 10/90% CO_2/N_2 atmosphere. In Leach 3 (L3), rock samples were reacted with 30% H_2O_2 (70% DI) under a 10/90% CO_2/N_2 atmosphere. Aside from the differences noted above, the operational procedure for generating leachates followed the same steps. First, 10.00±.05 g of pulverized rock (<0.5-mm sieve size) was added to an Erlenmeyer 125 mL flask followed by 20 mL of the extractant solution. Addition of DI water in L1 and L2 was done rapidly in one aliquot. Addition of H_2O_2 in L3 was done slowly by adding 1 mL at a time to reduce bubbling caused by oxidation reactions. Flasks were then placed on a shaker table inside a controlled atmosphere apparatus. The lid of the controlled atmosphere apparatus was left open for L1 or sealed for L2 and L3. For the sealed conditions, 10/90% CO_2/N_2 gas was constantly flushed through the apparatus. All extractions were shaken for 4 hours at 50 rpm and 20-22^{o}C. After 4 hours, each sample was filtered through a 0.45-µm cellulose acetate filter and pH and specific conductance (SC) of the filtrate were measured immediately (Oakton multiparameter PCTestr 35, calibrated with standards and buffers at 20-22^{o}C). The filtrate was transferred to a 100 mL volumetric flask and DI water was added to dilute the leachate to a final volume of 100 mL for analysis of elemental concentrations. Blank samples were prepared with DI water or H_2O_2 and followed all steps described above.

The strontium leach (L4) was prepared by extracting the rock samples three times using DI water. First, 2.0 g of pulverized rock (<0.5-mm) was added to 15 mL of DI water, shaken for 24 hours using a multi-tube vortexer and centrifuged for 20 minutes at 3,000 rpm. The supernantant was removed, 15 mL of DI water was added to the rock pellet, and the extraction was repeated two more times. The three supernatants were combined, filtered (0.45-µm cellulose acetate), and preserved with nitric acid. $^{87/86}Sr$ was separated from leachates using Sr Spec Eichrom Resin and nitric acid (2 N) to yield 0.1 to 1 µg of strontium. Separated strontium was analyzed on a ThermoFisher scientific Triton Plus thermal ionization mass spectrometer (TIMS) located at Penn State University EESL. Strontium was also extracted from NIST SRM 987 and IAPSO seawater standards and analyzed for $^{87/86}Sr$ as reference standards.

2.4 Analytical Methods

A suite of analytes were measured for each of the three leachates (Supporting Information Tables SI-1 – SI-3). SC and pH were measured with electrodes submerged in the undiluted leachate. Major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si) were measured after dilution to 100 mL on a Thermo Scientific iCAP 7400 inductively coupled plasma optical emission spectrometer (ICP-OES). Minor elements (As, Ba, Co, Cu, Li, Mo, Ni, Pb, Se, Sr, Th, Tl, Ti, U, V, Y, Zn, Zr) were measured on an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS). Anions (Br, Cl, NO_3, SO_4) were measured on a Dionex DX-120 ion chromatograph (IC). Total inorganic carbon (TIC) was determined by infrared detection after persulfate oxidation (ASTM, 2017). ABA parameters were determined by standard methods (Sobek et al. 1978). Total sulfur was analyzed by dry combustion, and maximum potential acidity (MPA) was calculated by multiplying total S (%) by 31.25 to obtain g kg^{-1} $CaCO_3$

equivalent. Neutralization potential (NP) was determined by reacting samples with HCl and titrating the effluent with NaOH using methods of Noll et al. (1988), without modification to account for siderite (Skousen et al., 1997). Net neutralization potential (NNP) was calculated by subtracting MPA from NP; negative NNP values imply a potentially acid-producing sample. The above analyses were conducted at Geochemical Testing, Somerset, PA. $^{87}Sr/^{86}Sr$ ratios were measured on a thermal ionization mass spectrometer (TIMS) located at the Penn State University Energy and Environmental Sustainability Laboratories. Radium isotopes (^{226}Ra, ^{228}Ra) were measured using a small anode germanium detector gamma spectrometer from Canberra Instruments at geometries consistent with internal standards and certified reference materials (UTS-2). After a 21 day equilibration, ^{226}Ra was calculated from the average activity of Bi-214 (609 keV) and Pb-214 (295 & 351 keV). Direct measurement of ^{228}Ra were performed using its ^{228}Ac daughter at 911 keV.

Mineralogy of the rock samples were characterized by X-ray diffraction (XRD) using a PANalytical X'Pert 165 PRO MPD X-ray diffractometer equipped with a PIXcel detector operated in a 1D scanning mode with all channels active. Samples were subjected to Cu K-α radiation from 5 to 70 degree (2θ) at 45 kV and 40 mA. Semi-quantitative analyses were performed using whole pattern fitting in Jade 2010 software from Materials Data Incorporated of Livermore, CA in conjunction with reference files from the International Centre for Diffraction Data PDF4 database. Mineral detection limits were about 3% (m/m) and uncertainty in mineral fractions were ±5%.

2.5 Speciation Modeling Methods

The PHREEQC 3.0 aqueous speciation model (Parkhurst and Appelo, 2013) was used with input values for leachate data, corrected for dilution (100/volume leachate recovered), to estimate SC by methods reported by McCleskey et al. (2012) and Appelo et al. (2010) as described by Cravotta and Brady (2015). Input data to PHREEQC included the sample temperature, pH, and the mass concentrations (mg/L) of TIC, SO_4, Cl, F, Br, NO_3-N, P, Si, Ca, Mg, Na, K, Li, Fe, Mn, Al, Ba, Sr, and Zn in the filtered leachates. Both methods calculated SC using the same speciated cations and anions (H^+, Li^+, Na^+, K^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, F^-, Cl^-, Br^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_3^- , and OH^-), trace metals (Al^{3+}, Fe^{2+},

Fe^{3+}, Mn^{2+}, and Zn^{2+}), and charged ion pairs (HSO_4^-, $NaSO_4^-$, $NaCO_3^-$, and KSO_4^-), however, the computations used to determine ionic conductivities were different. Briefly, the Appelo et al. (2010) method calculates the ionic conductivity of solute species using ion diffusion coefficients while the McCleskey at al. (2012) method calculates ionic molal conductivities using transport numbers. Both methods sum the ionic conductivity contributions to indicate the solution SC. Additional details on the SC computations are provided in the Supporting Information.

The concentration of total dissolved solids (TDS) was computed as the sum of the input concentrations of major dissolved constituents (Ca, Mg, Na, K, SO_4, Cl, CO_3, NO_3, SiO_2) (Fishman and Friedman, 1989) plus minor constituents (Sr, Ba, Fe, Al, Mn, Br), assuming that Fe, Al, and Mn formed hydrous oxides (FeOOH, AlOOH, MnOOH) instead of anhydrous compounds. Cravotta and Brady (2015) showed that TDS values computed accordingly were comparable to the laboratory measured residue on evaporation at 180 ºC for mine effluent samples. Osmotic pressure (OP) was computed as the sum of molal concentrations of the same aqueous species used for SC calculations. The OP computation assumes that 1 mol/kg of each ion exerts approximately 1 mOsm/kg osmotic pressure (Haynes et al., 2013). Cravotta and Brady (2015) showed that computed values of OP for mine effluent samples were comparable to standard laboratory measured values of OP using freezing point depression (Kiyosawa, 2003).

2.6 Data for Upscaling Comparisons

Several of the rock samples characterized by operational batch extractions were previously used in laboratory-scale flow-through column experiments or obtained from field sites with paired water samples (Table 1). For upscaling batch extractions to column experiments, sixteen overburden and three weathered coal refuse samples were compared using mass-normalized TDS. As TDS was not reported for column experiments (only SC), a SC-to-TDS conversion factor (CV = TDS/SC = mg TDS L^{-1}/μS cm^{-1}) was calculated for each paired sample using the SC measured in L1 and the corresponding TDS value calculated using the input concentrations for PHREEQC (Supporting Information Table SI-4). The cumulative TDS generated in the column experiment following approximately 14 or 40 discontinuous leaching events was calculated according to:

$$Cumulative\ column\ leached\ TDS\ \left(\frac{mg\ TDS}{L}\right) = \frac{\sum_{n=1}^{i}(SC_i \times V_i \times CV)}{V_{total}} \qquad \text{Eq 1}$$

where, SC_i = SC measured from i-th leach event (µS cm^{-1}); V_i = volume of each leach event (L); CV = rock-specific SC-to-TDS conversion factor (mg TDS L^{-1}/µS cm^{-1}), and V_{total} = total volume of leaches (L).

Comparisons between field sites and batch experiments were made based on SC, as this parameter was reported for all field samples. A total of ten field sites were included (referred to as Mine A, Mine B, Mines P, KY1, KY2, KY3, KY9, LKFC, BCS3, Skytop), where SC measured from a select number of rock samples were paired with a varied number of SC values measured in the field. For Mine A, 42 records of SC and additional analytes from leachate drains were compared to five weathered coal refuse samples collected from Mine A. For Mine B, 41 records from leachate drains were compared to six weathered coal refuse samples collected from Mine B. For Mines A and B, records were obtained from a field sampling event in March 2017 and from Hydrologic Monitoring Reports (HMRs) submitted by the coal companies to the Pennsylvania Department of Environmental Protection. For Mines P, three records from influent discharges to three Pittsburgh Coal mining/processing plants on active underground mines (Cravotta and Brady, 2015) were compared to 17 unleached coal refuse samples stratigraphically adjacent to the Pittsburgh Coal Formation (TGS1-TGS17, Table 1). Field results for KY1-KY3 are summarized by Sena et al. (2014). For KY1, 199 records from field lysimeters built on top of a valley fill were compared to rock sample KY1 (unweathered overburden). For KY2, 110 records from field lysimeters built on top of a valley fill were compared to rock sample KY2 (unweathered overburden). For KY3, 203 records from field lysimeters built on top of a valley fill were compared to rock sample KY3 (unweathered overburden). For KY9, 18,064 records from a leachate drain at the toe of two valley fills were compared to rock sample KY9 (unweathered overburden). Three records from influent discharges from coal processing plants (Cravotta and Brady, 2015) and 24 records from discharges from abandoned mines in the Lower Kittanning Formation (Cravotta, 2008) were compared to rock sample LKFC (unweathered overburden). Six records from influent discharges from active mines (Cravotta and Brady, 2015) and 10 records from discharge samples from abandoned mines in the Lower to Upper Freeport Formations (Cravotta, 2008) were compared to rock sample BCS3 (unweathered overburden). Four records from drainage from the Skytop roadcut collected in May 2004 (Hammarstrom et al., 2005) were compared to rock sample SKYPA (pyrite).

2.7 *Statistical Methods*

Statistical differences between batch extractions (L1, L2, and L3) and upscaled results for selected parameters were evaluated using the Wilcoxon-signed rank test. Outliers were defined as values greater than the 75th percentile plus 1.5 times inter-quartile distance, or values smaller than the 25th percentile minus 1.5 times inter-quartile distance. SC and TDS were compared via correlation (Pearson) analyses. Comparisons between TDS from leaches were compared with TDS from column experiments using Pearson correlation and by comparing the fit of our data (R^2) with the line of equality y = x. SC data from the field were compared with SC from batch extractions using an unpaired t-test. Linear regression equations were generated for each rock category and for the full data set. R was used for all statistical analyses (R Core Team, 2016).

3. RESULTS AND DISCUSSION

3.1 *Comparison of Operational Extractions*

Three operational extractions were designed to have varying reactivity with sulfides, carbonates, silicates, sulfates, and salts. DI water alone (L1) was presumed to extract weakly-held exchangeable ions, salts, hydrolysis products, and high-solubility minerals. The equilibration of the DI extractant with 10% CO_2 atmosphere (L2) was hypothesized to promote carbonate dissolution. Although the pH of the L2 extractant blank was less than that of L1, as described below, this level of CO_2 did not create significant changes in the chemistries of leachates produced by L1 versus L2. In contrast, the 30% H_2O_2 in L3 promoted sulfide oxidation, and the production of sulfuric acid promoted the dissolution of many other minerals. Relationships between SC, TDS, pH, and TIC reflect the major reactions promoted by the extractant solutions. For example, for rocks with high sulfide and low carbonate contents (as determined by XRD), the increase in SC and TDS after the addition of H_2O_2 (i.e., L1 vs L3) was dominated by production of SO_4^{2-} and H^+. As another example, for rocks with low sulfide and high carbonate contents, the increase in SC and TDS after reaction with CO_2 (i.e., L1 vs L2) was controlled by release of Ca^{2+} and HCO_3^-.

Chemistry data for all rock samples are provided as Excel files in Supporting Information Tables SI-4 (leachates), SI-5 (blanks), and SI-6 (solids). For the blanks, the median (and range) of pH values were: L1, 6.0 (4.1 – 7.0, n=7); L2, 5.1 (4.4 – 6.3, n=5); and L3, 2.6 (1.8 – 4.5, n=7). The median measured SC values for the blanks were 13 µS/cm (5.0 – 85, n=7), 45 µS/cm (15 – 90, n=5), and 227 µS/cm (33 – 973, n=7) in L1, L2, and L3, respectively. The median calculated TDS values for the blanks were 26 mg/L (16 – 223, n=7), 30 mg/L (14 – 34, n=5), and 138 mg/L (26 – 339, n=7) in L1, L2, and L3, respectively.

Operational extractions L1, L2, and L3 were compared based on pH, TDS and SC results from all rock samples (Figure 1). The D'Agostino & Pearson normality test showed that the measured values for these parameters did not follow a normal distribution, therefore, comparisons between leachates were made using the Wilcoxon-signed rank test. This test showed that SC (measured and calculated), TDS, and pH values were significantly different (at 95% confidence) in L3 compared with L1 and L2, and that differences between L1 and L2 were not significant (Supporting Information Table SI-7). In general, L3 showed an increase in SC and TDS and a decrease in pH compared with L1 (Figure 1B,D,F). As noted above, this was the result of the oxidation of sulfide minerals promoted by the use of H_2O_2 in L3. The decreased pH promoted the dissolution of carbonate minerals and release of HCO_3^-, Ca^{2+}, and other ions into solution. Most of the samples showed a substantial increase in SC in L3 compared to L1 (Figure 1B). However, six samples showed only a modest increase in SC (samples touching line of equality in Figure 1B). These six samples contained high sulfate and low sulfide contents where the sulfate salts were quickly dissolved by water and the addition of H_2O_2 did not greatly enhance mineral dissolution. Of these six samples, four were unleached coal refuse (TGS 2A, TGS8, TGS10A, and TGD10B), one was weathered coal refuse (TNR2), and one was shale (SOH1). Consistent with statistical paired tests, results

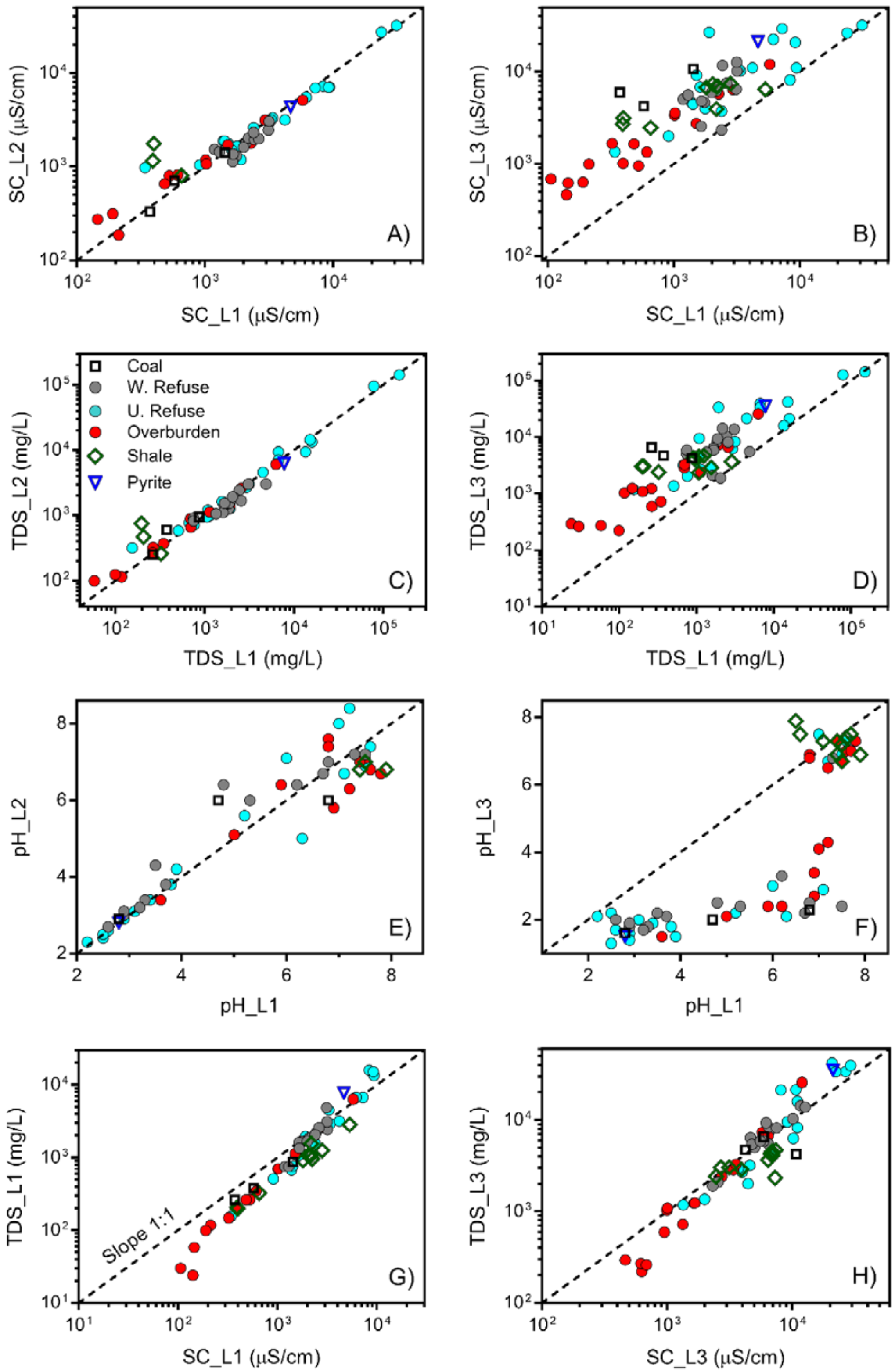


Figure 1. Comparisons between different batch extractions. Panels A, C and E (n=59) show correlations between Leach 1 (L1) and Leach 2 (L2). Panels B, D, and F (n=63) show correlations between L1 and Leach 3 (L3). Panels G and H (n=63) show correlations between SC and TDS in L1 and L3.

from L1 and L2 were similar (Figure 1A,C,E). However, five samples showed an increase in SC in L2 compared to L1 (Figure 1A). Of these five samples, two were gas-producing shales (SHM2, SHM3), one was unweathered coal refuse (TGS13), and two were sandstone overburden (VA16, WV5). The first three samples had abundant calcite and minor pyrite (Table 1). Although neither mineral was detected by XRD for VA16 or WV5 (Table 1), the two overburden samples had detectible NP and S (Table S3). In any case, the added CO_2 in L2 appears to have enhanced carbonate dissolution.

The majority of pH values for L3 were lower than L1 (Figure 1F) because of enhanced sulfide oxidation by H_2O_2+CO_2. However, a large number of samples (23 of 65) with pH values ranging from 6.5 to 7.9 (samples clustered in upper right of Figure 1F) exhibited little change in pH in L1 versus L3. These samples contained high carbonate and low sulfide contents, with corresponding positive values of NNP (Table 1 and Supporting Information Table S6), and produced enough alkalinity to neutralize the sulfuric acid produced. Of these twenty-three samples, eight were shales, six were unleached coal refuse, two were weathered coal refuse, and seven were overburden.

For the six rock types, median values for pH, SC, TDS, and OP were used to compare L1 and L3 (Figure 2). In general, pyrite and unleached coal refuse produced the highest median values for SC and TDS while overburden produced the lowest median values. Median values for these parameters from weathered coal refuse, coal, and shale always ranked in intermediate positions, although the order switched depending on the analyte or extraction method. For instance, the order for TDS (mg/L) in L1 was pyrite (7,770) > unleached coal refuse (2,430) > weathered coal refuse (1,870) > shale (1,020) > coal (375) > overburden (262), while the order in L3 was pyrite (35,200) > unleached coal refuse (8,920) > weathered coal refuse (6,160) > coal (4,700) > shale (3,360) > overburden (1,080). Median values of TDS and SC in L3 were all higher than corresponding proposed regulatory reference levels, 500 mg/L and 300 – 500 µS/cm (Cormier et al., 2013a, 2013b; Pond et al., 2008; Timpano et al., 2010), respectively, for all rock types. Except for overburden, median values of OP in L3 were all higher than the regulatory reference level of 50 mOsmol/kg (Commonwealth of Pennsylvania, 2018b).

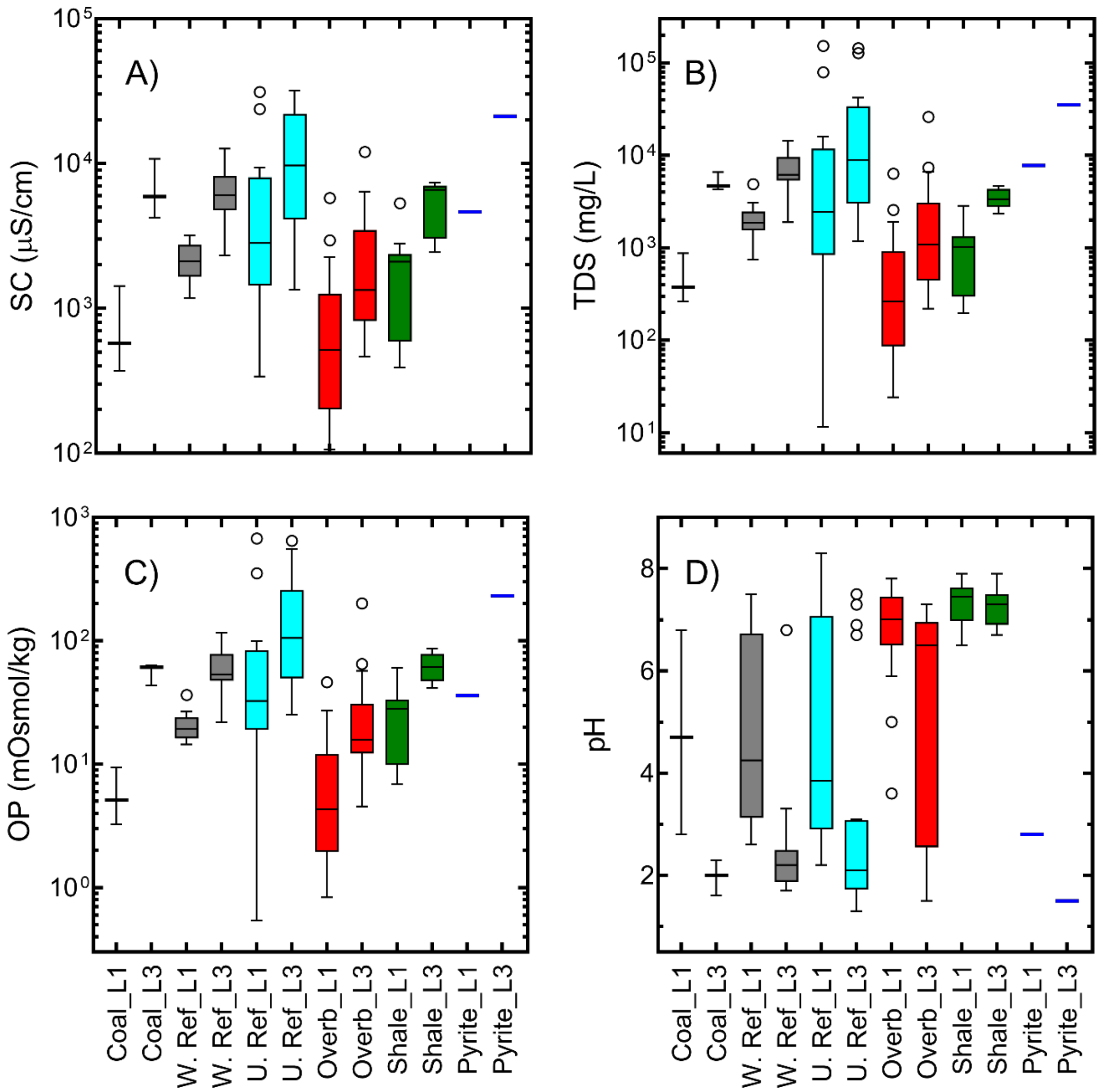


Figure 2. Summary of chemistry for Leach 1 (L1) and Leach 3 (L3) for the six rock types. Coal (n=3); Weathered Coal Refuse = W. Ref (n=14); Unleached Coal Refuse = U. Ref (n=20); Overburden = Overb (n=17); Shale (n=10); Pyrite (n=1). Box plots show median, 25% and 75% quartile ranges. Whiskers show the minimum and maximum values. Outliers (circles) defined as any point at a distance greater than 1.5 times the interquartile range measured from the 75^{th} to the 25^{th} percentile.

It is important to note that our results for TDS from Marcellus and Utica/Point Pleasant Shale are not consistent with values reported for waters produced from unconventional gas wells drilled into these formations. For instance, Tasker et al. (2019) reported median values of TDS of 240,000 mg/L for Utica/Point Pleasant Shale wells (n=24) and 225,000 mg/L for Marcellus Shale wells (n=60). Those values are nearly two orders of magnitude greater than the median TDS obtained for gas-bearing shales with our most aggressive extractant (TDS_L3 = 3,360 mg/L). Produced water from hydraulically fractured shale gas wells could encounter extensive small fracture networks equivalent to exceptionally low water-to-rock ratios or could interact with brines that were not within (or preserved) in our samples. This is consistent with other studies that have shown TDS values from batch extractions of Marcellus Shale are much lower than corresponding field produced waters (Chapman et al., 2012; Phan et al., 2015; Rowan et al., 2011; Stewart et al., 2015, 2014; Tasker et al., 2016; Warner et al., 2012).

3.2 Leachate Composition

The median concentrations of dissolved metals, metalloids, and anions varied based on rock type, weathering extent, and final pH of the extract (Figure 3). Based on sample mineralogy and leachate composition, the principal mechanisms for TDS generation are oxidation of sulfide minerals (with production of H_2SO_4) that promotes increased solubility of metals (e.g., Fe, Al, Mn), dissolution and hydrolysis of carbonate and silicate minerals to neutralize acidity, and dissolution of high-solubility minerals such as sulfates and salts. Because of its high organic carbon content, coal contained relatively low concentrations of metals. Based on XRD (Table 1), coal samples contained quartz, calcite, clays, and pyrite. Concentrations of Si, Ca, Al, Fe, and SO_4 in the coal leachates are consistent with this mineral assemblage.

Weathered coal refuse had been exposed to shallow subsurface weathering for years, while rock cores classified in this study as unleached coal refuse had been exposed to humid air only while archived in core boxes. These differences in weathering extent led to distinct differences in leachate chemistry. Unleached coal refuse released higher alkali metals, notably Na, and higher Cl compared to weathered coal refuse (Figure 3), reflecting that salts had been preserved in storage. Plots of Cl versus Na molar concentrations in both L1 and L3 showed that only the shale samples consistently plotted along the 1:1 line of equality supporting the assumption of NaCl dissolution (Supporting Information Figure SI-1). Na was also likely sourced from exchange reactions and silicate neutralization. Unleached coal refuse also released higher SO_4, notably in L3, compared to weathered coal refuse, reflecting that some sulfides had

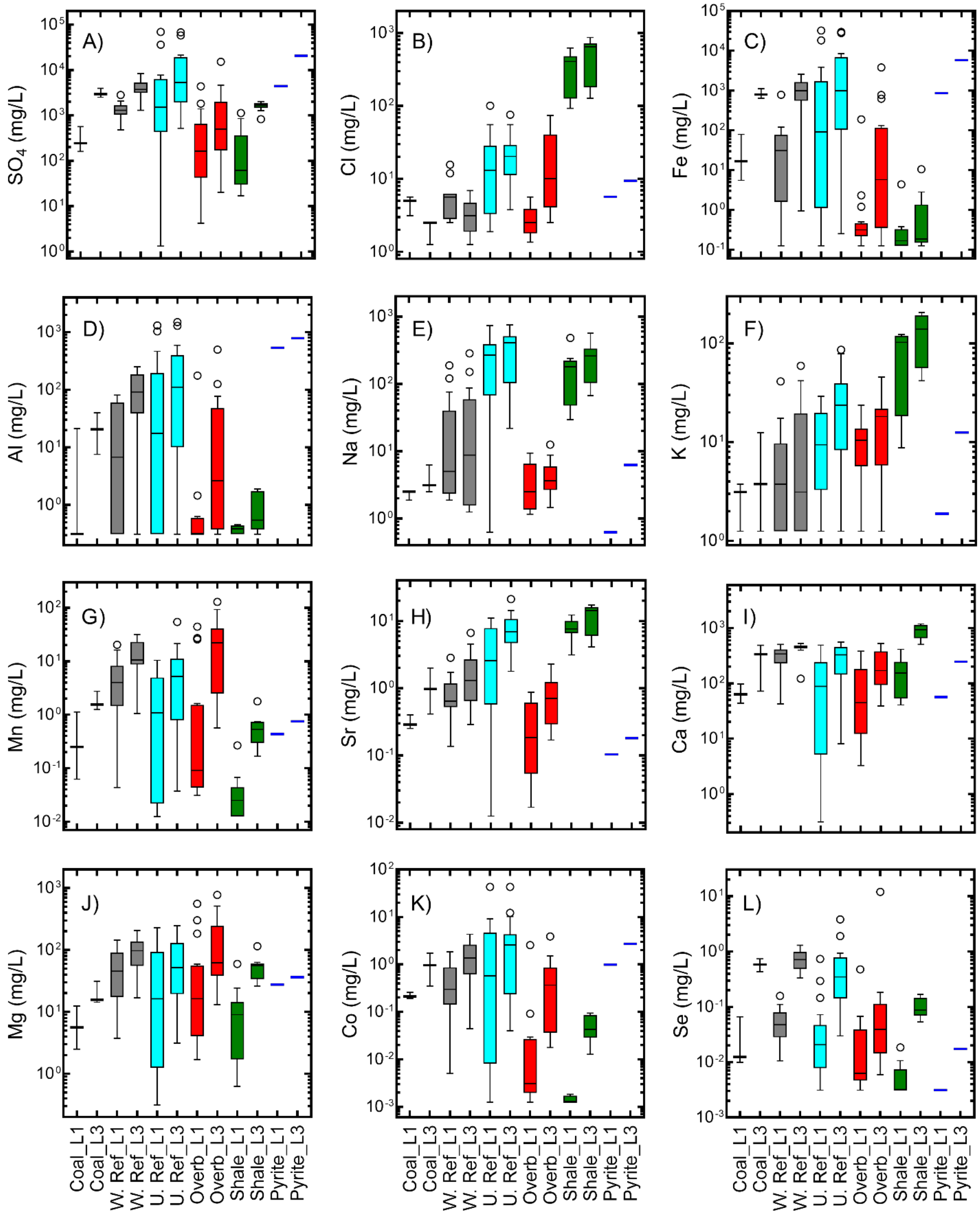


Figure 3. Summary of chemistry for Leach 1 (L1) and Leach 3 for the six rock types. Coal (n=3); Weathered Coal Refuse = W. Ref (n=13 or 14); Unleached Coal Refuse = U. Ref (n=20); Overburden = Overb (n=17); Shale (n=10); Pyrite (n=1). Box plots show median, 25% and 75% quartile ranges. Whiskers show the minimum and maximum values. Outliers (circles) defined as any point at a distance greater than 1.5 times the interquartile range measured from the 75th to the 25th percentile.

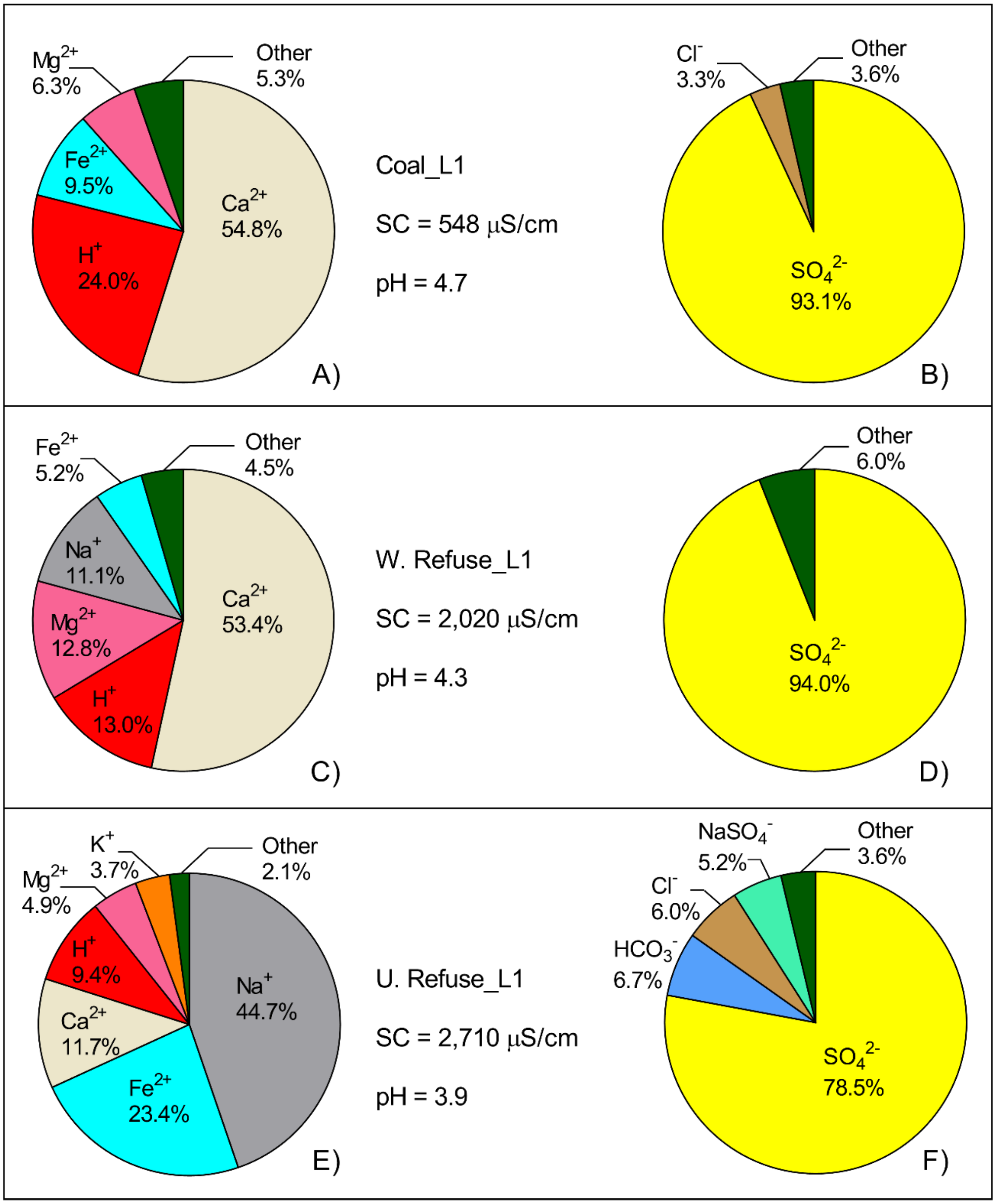
not been oxidized during core storage. Concentrations of transition metals and Se were similar between unleached and weathered coal refuse (Figure 3).

Differences in mineral composition (Table 1) of overburden, shale, and pyrite help explain differences in leachate chemistry. In L3, overburden samples released low alkali metals and chloride, reflecting low entrained salt content, and low SO_4 reflecting low sulfide content. Gas-bearing shale samples released high alkali metals and the highest amounts of Cl and Br, reflecting relatively high salt content, low SO_4 reflecting low sulfide content, and high alkaline earth metals, notably Sr and Ba, reflecting high carbonate content. The sole pyrite sample released the highest amounts of Fe, SO_4, Al, Pb, Zn, and As reflecting high sulfide content.

3.3 Contribution of ionic species to specific conductance

The relative contributions of ionic species to the SC were calculated for all rock types in L1 and L3 using the method of McCleskey et al. (2012). For L1, the major cationic contributions to SC were Ca^{2+} > Na^+ > Mg^{2+} > Fe^{2+} > H^+ > K^+, and major anionic contributions to SC were SO_4^{2-} > Cl^- > HCO_3^- (Figures 4 and 5). However, the rank of ion contributions to SC differed slightly depending on rock type. For instance, Ca^{2+} was the dominant cation in coal, weathered coal refuse, overburden, and gas-bearing shale, but Na^+ was the dominant cation in unleached coal refuse and Fe^{2+} was the dominant cation in pyrite. On the other hand, the anionic contributions to SC were dominated by SO_4^{2-} for all rock types except for gas-bearing shale, where Cl^- was most abundant. The high contribution of Cl^-, Na^+, and Ca^{2+} to SC in gas-bearing shales (Figure 4I, J) provide evidence for salt dissolution. The general contribution of principal cations and anions to SC in L1 were consistent with the mechanisms of TDS generation discussed above.

With the addition of H_2O_2 to L3, sulfide oxidation and the consequent release of sulfuric acid became an important mechanism for ion mobilization by mineral dissolution. While the major ions that contribute to SC in L3 were similar to those in L1, the contribution of H^+ increased markedly in L3 (Figure 5). The major cationic contributions to SC in L3 were H^+ > Ca^{2+} > Fe^{2+} > Na^+ > Mg^{2+} > K^+. Anionic contributions to SC in L3 were dominated by SO_4^{2-} > HSO_4^- > Cl^- > HCO_3. Na^+ was an important contributor to SC from unleached coal refuse and gas-bearing shale. The increased release of Na^+ from



Mg2+ 6.3%
Other 5.3%
Fe2+ 9.5%
Ca2+ 54.8%
H+ 24.0%
A)
Coal_L1
SC = 548 µS/cm
pH = 4.7
Cl- 3.3%
Other 3.6%
SO42- 93.1%
B)
Fe2+ 5.2%
Other 4.5%
Na+ 11.1%
Ca2+ 53.4%
Mg2+ 12.8%
H+ 13.0%
C)
W. Refuse_L1
SC = 2,020 µS/cm
pH = 4.3
Other 6.0%
SO42- 94.0%
D)
K+ 3.7%
Other 2.1%
Mg2+ 4.9%
H+ 9.4%
Na+ 44.7%
Ca2+ 11.7%
Fe2+ 23.4%
E)
U. Refuse_L1
SC = 2,710 µS/cm
pH = 3.9
NaSO4- 5.2%
Other 3.6%
Cl- 6.0%
HCO3- 6.7%
SO42- 78.5%
F)

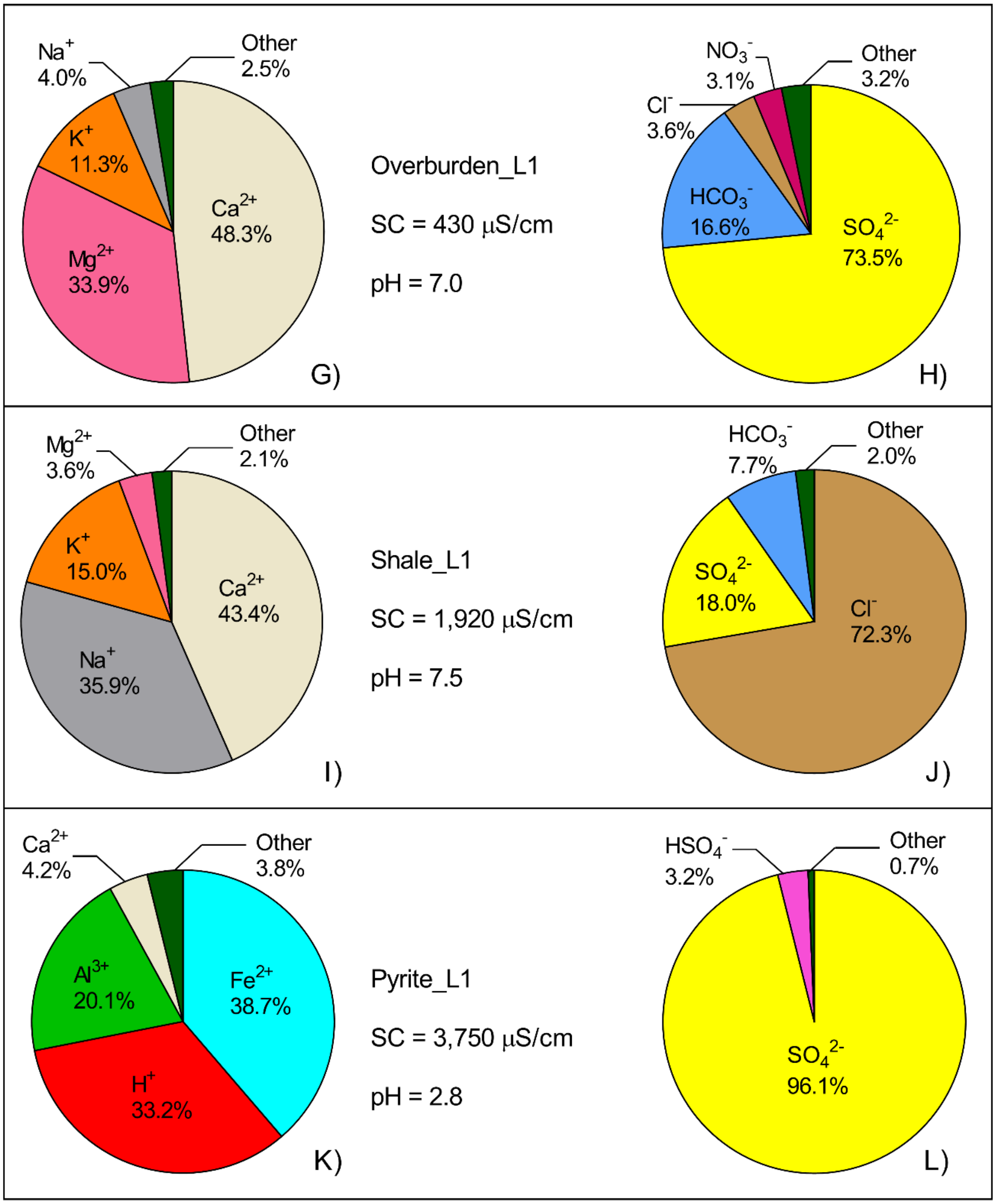
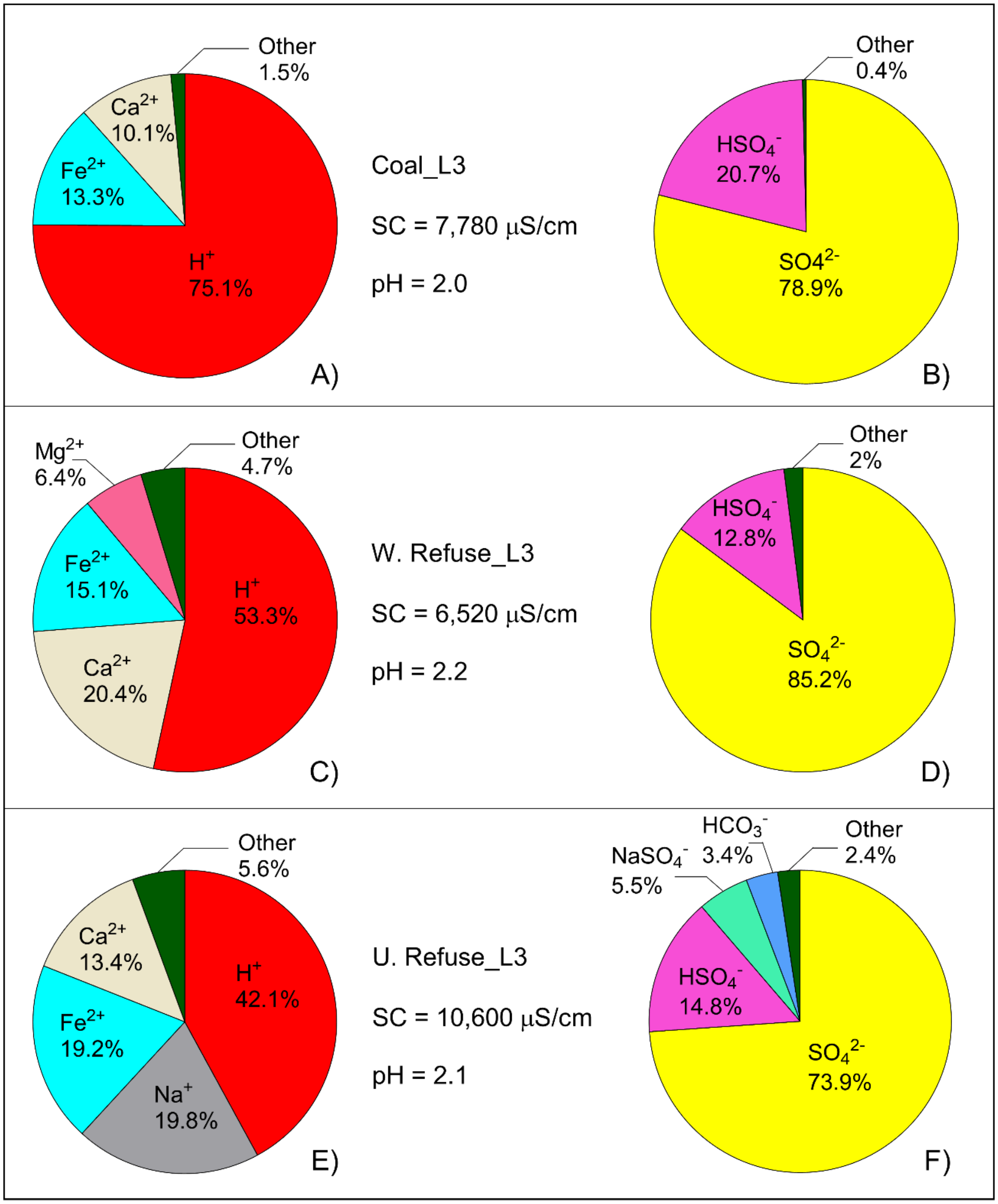


Figure 4. Ionic contributions to specific conductance in Leach 1 (L1). Median specific conductance (SC), and ionic contributions calculated according to McCleskey et al. (2012). Median pH is shown for each rock category. Left panels show cationic contributions normalized to median SC for each rock category. Right panels show anionic contributions normalized to median SC for each rock category. Coal (n=3); Weathered Coal Refuse = W. Refuse (n=14); Unleached Coal Refuse = U. Refuse (n=20); Overburden (n=17); Shale (n=10); Pyrite (n=1).



Other
1.5%
Ca2+
10.1%
Fe2+
13.3%
H+
75.1%
A)
Coal_L3
SC = 7,780 μS/cm
pH = 2.0
Other
0.4%
HSO4-
20.7%
SO42-
78.9%
B)
Mg2+
6.4%
Other
4.7%
Fe2+
15.1%
H+
53.3%
Ca2+
20.4%
C)
W. Refuse_L3
SC = 6,520 μS/cm
pH = 2.2
Other
2%
HSO4-
12.8%
SO42-
85.2%
D)
Other
5.6%
Ca2+
13.4%
H+
42.1%
Fe2+
19.2%
Na+
19.8%
E)
U. Refuse_L3
SC = 10,600 μS/cm
pH = 2.1
HCO3-
3.4%
NaSO4-
5.5%
Other
2.4%
HSO4-
14.8%
SO42-
73.9%
F)

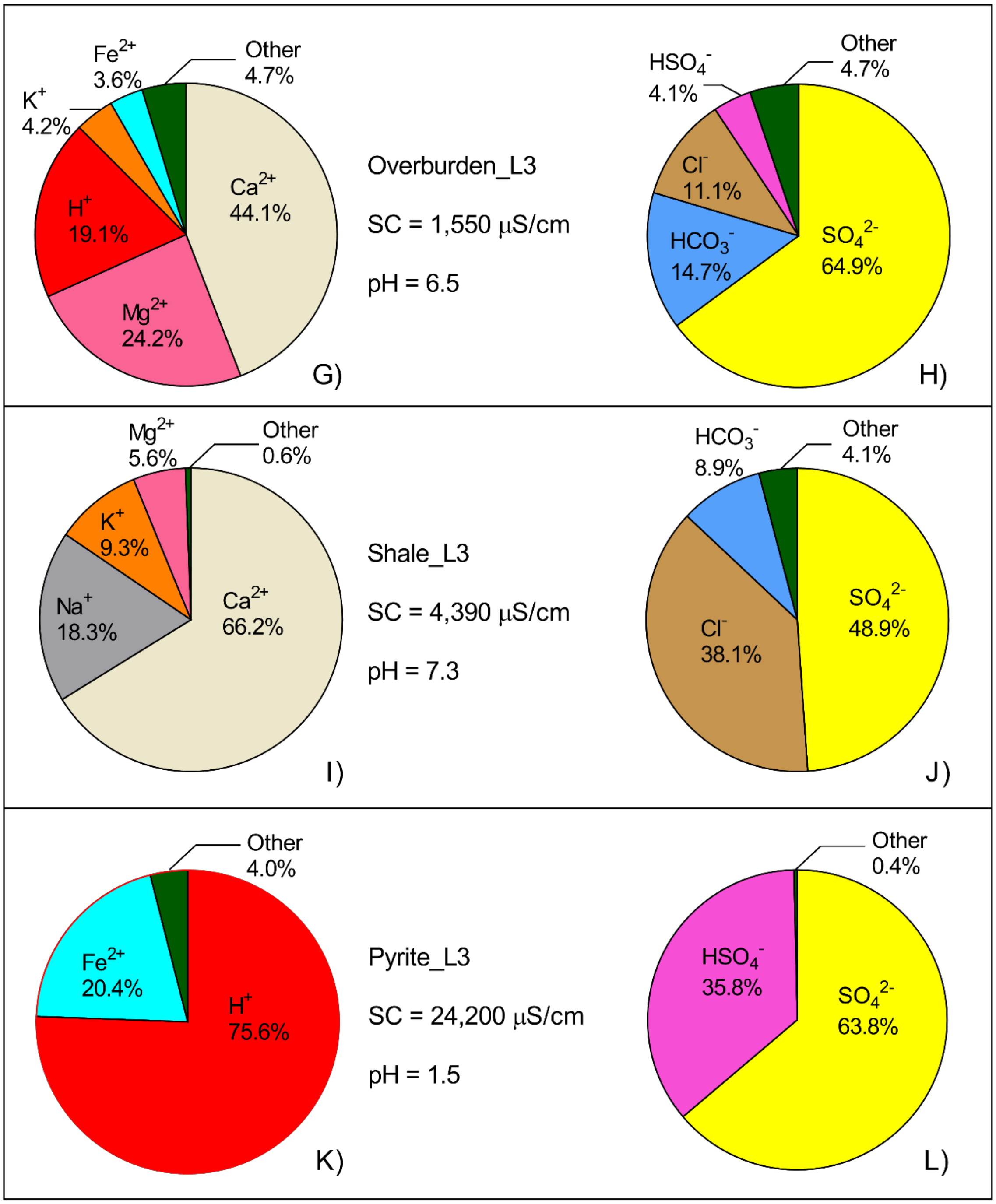


Figure 5. Ionic contributions to specific conductance in Leach 3 (L3). Median specific conductance (SC), and ionic contributions calculated according to McCleskey et al. (2012). Median pH is shown for each rock category. Left panels show cationic contributions normalized to median SC for each rock category. Right panels show anionic contributions normalized to median SC for each rock category. Coal (n=3); Weathered Coal Refuse = W. Refuse (n=14); Unleached Coal Refuse = U. Refuse (n=20); Overburden (n=17); Shale (n=10); Pyrite (n=1).

gas-bearing shale with L3 compared to L1 is consistent with silicate mineral decomposition combined with salt dissolution. Cl^- was an important contributor to SC of L3 only from gas-bearing shale, where the SO_4^{2-} release was greater than Cl^-. Mg^{2+} and HCO_3^- were important contributors to SC only from overburden. Although pH of L3 remained near-neutral for the gas-bearing shale and overburden, the increased release of SO_4^{2-}, Ca^{2+}, and Na^+ with L3 compared to L1 demonstrates the importance of mineral decomposition in conjunction with pyrite oxidation, acidification, and neutralization.

3.4 Upscaling from lab to field

An important part of this study was to test the capability of the proposed rapid batch extractions on 10 g samples for predicting TDS release from coal refuse and overburden of larger size and at longer time scales. Available information from previous column studies and water quality data from ten field sites were compared with our batch extractions. Seventeen overburden samples and three weathered coal refuse samples (Table 1) were previously analyzed in column studies (Agouridis et al., 2012; Daniels et al., 2009; Daniels et al., 2016; Daniels et al., 2014b; Hornberger and Brady, 2009; Odenheimer et al., 2015; Sena et al., 2014). In general, all column studies maintained unsaturated conditions with simulated rainfall (pH 4.6) leaching events. The number and frequency of leach events, the rainfall volume, and the rock mass in the columns varied between experiments conducted by Daniels et al. (2016) versus Hornberger et al. (2009). Daniels et al. (2016) constructed columns with 1,200 cm^3 (~1,800 g) of rock and applied 125 mL of synthetic rain water twice a week for a total of 40 leach events. Hornberger et al. (2009) constructed columns with 1,300 to 2,100 grams of rock and applied 190 to 650 mL of synthetic rain water once a week for a total of 14 leach events. As described below, the overall water volume (sum of individual leaches) to rock mass ratio strongly controls leachate chemistry. As these two groups of researchers ultimately used similar water-to-rock ratios in their column studies, results from all studies are comparable when normalized to rock mass. In general, SC in the column leachates started at the highest values, declined in an exponential manner, and then approached an asymptotic minimum. Comparisons with batch experiments were made based on cumulative TDS calculated from the column experiments. Column leachate data were compiled as SC and then converted to TDS, based on rock-specific correlations derived from L1, using Eq 1. Based on this approach, we found that TDS from batch extraction L1 and cumulative TDS calculated from column experiments were well correlated (Figure 6). These batch and column methods likely produced similar amounts of cumulative TDS because the water-to-rock ratios used in all experiments were of similar order of magnitude (2 mL-to-1 g in batch experiments vs 2.5 mL-to-1 g to 3.2 mL-to-1 g in column experiments), and the smaller particle size used in the batch extractions (≤ 0.5-mm for batch experiments versus ≤ 2-mm to ≤ 1.25-cm for column experiments) may promote more rapid release of TDS. However, overburden samples that produced the lowest amounts of TDS in L1 produced more cumulative TDS via column leaching (lower left of Figure 6A).

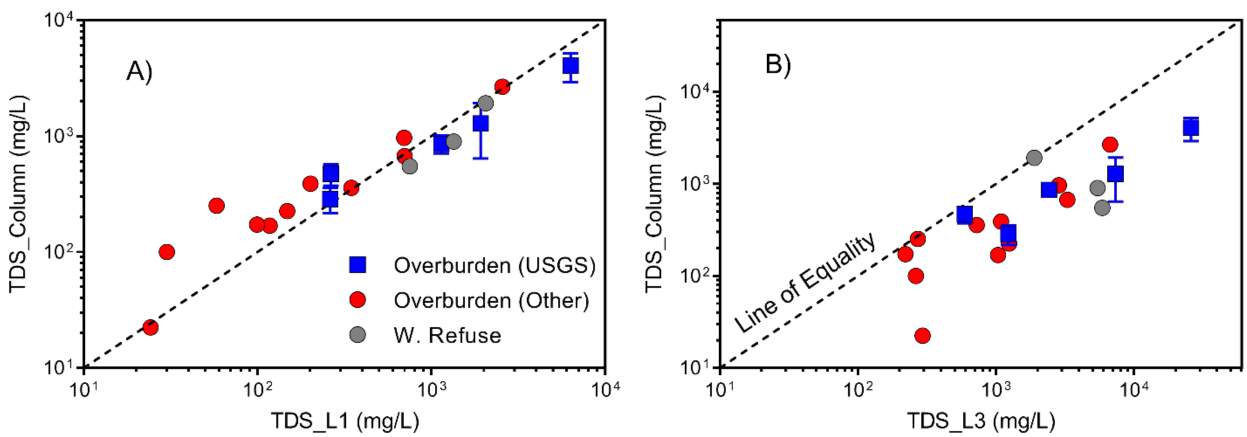


Figure 6. Cumulative total dissolved solids (TDS) calculated for column experiments (calculated using Eq. 1) versus TDS measured in Leach 1 (L1) and Leach 3 (L3). For column experiments with replicates, symbols represent mean values and error bars represent standard deviation. Error bars smaller than the symbol size are not shown. Weathered coal refuse = W. Refuse (n=3). Overburden samples donated by USGS = Overburden (USGS) (n=5), overburden samples from other sources = Overburden (Other) (n=11).

TDS from batch extraction L3 tended to overpredict cumulative TDS calculated from the column experiments (Figure 6B; Supporting Information Table SI-8). These results suggest that even multiple column leaching events cannot achieve the extractive strength of H_2O_2+CO_2 used in batch extraction L3. Furthermore, these results suggest that multiple discontinuous rainfall leaching events do not substantially increase the extractive strength of synthetic rain (or physical access to additional reactive sites), and that the cumulative water-to-rock ratio exerts greater control on leachate chemistry for water extractions.

In contrast to the column experiments, field SC was better correlated to SC from batch extraction L3 versus L1 (Figure 7; Supporting Information Table SI-9). Field data and batch extractions were compared for nine of the 10 field sites using an unpaired t-test (not enough data were available to test the other three sites). Seven of the nine sites showed no statistical differences between field SC and L3 SC. We note that field SC values from rock disposal facilities (a.k.a. excess spoil fills pursuant to SMCRA) change over time (Evans et al., 2014), and that the 'age' of the rock/leachate could not be controlled in this study. However, we chose to analyze all these sites together because they represent the largest, most analytically consistent data set available for addressing our research objectives. In contrast, five of the nine sites showed significant statistical differences between field SC and L1 SC, where SC results from L1 underestimated the field SC.

Collectively these upscaling comparisons suggest that weathering in the field is influenced by acid-formation and neutralization reactions that produce greater solute concentrations than simple dissolution of soluble salts and exchangeable ions by water alone. Column leaching experiments produce high SC in the first leaches but values decline rather quickly. Scaling up from column experiments to field sites is challenging for a number of reasons. One obvious issue is that coal refuse disposal fills often contain millions of cubic meters of rock such that the rock-to-water ratio is dramatically greater in the field as compared to tens of pore volumes eluted through laboratory columns. Unlike column experiments, water percolating through rocks stored in disposal fills may encounter multiple and much longer flow paths such that the water encounters more 'fresh' reactive material. Water may migrate through these rocks much slower and encounter many more wetting-and-drying cycles as compared to column experiments such that the field leachates oxidize more sulfides, generate a lower pH, and solubilize more metals. Rocks in disposal fills may also disaggregate over long periods of time, effectively increasing the rock-to-water ratio.

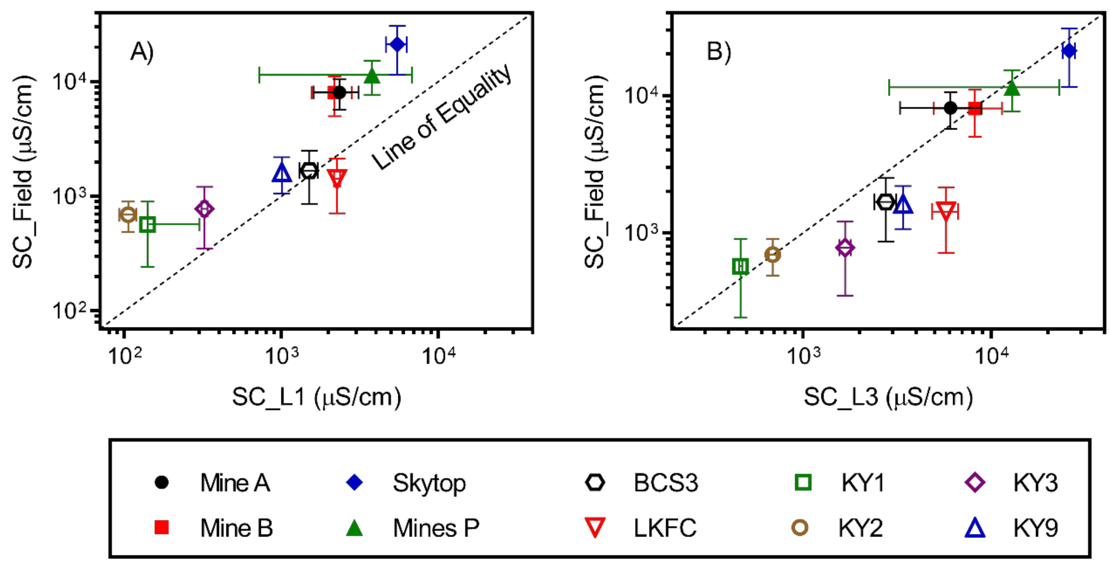


Figure 7. Relationships between specific conductance (SC) measured in the field and in A) Leach 1 (L1) and B) Leach 3 (L3). Symbols represent mean values and error bars represent standard deviation. For SC measured in the field: Mine A (n=42); Mine B (n=41); Mines P (n=3); KY1 (n=199), KY2 (n=110), KY3 (n=206), KY9 (n=18,064); LKFC (n=25); BSC3 (n=16); Skytop (n=4). For SC measured in L1: Mine A (n=5); Mine B (n=6); Mines P (n=17); KY1 (n=3); KY2 (n=3); KY3 (n=3); KY9 (n=1); LKFC (n=3); BSC3 (n=3); Skytop (n=8). For SC measured in L3: Mine A (n=5); Mine B (n=6); Mines P (n=17); KY1 (n=3); KY2 (n=3); KY3 (n=3); KY9 (n=1); LKFC (n=2); BSC3 (n=2); Skytop (n=14).

3.5 Correlations between SC and ABA parameters

Acid-base accounting (ABA) parameters are used to identify and segregate rocks with high acid generation potential (or blend with rocks with high alkalinity). The use of ABA parameters to identify TDS release potential would be cost-effective for coal mine operators, provided that the TDS predictions based on ABA were accurate. Of all the correlations between ABA parameters and analytes measured in L1 and L3 extracts, maximum potential acidity (MPA) displayed the most promising correlations with SC from L3 (Table 2). It was anticipated that MPA + NP might better predict TDS release, but this did not produce an improved relationship. While MPA is certainly correlated with TDS release, correlation coefficients were not high for all rock types and notably low for weathered coal refuse, plus different linear regression coefficients (slope and intercept) were indicated for different rock types (Supporting

Information Figure SI-2). Therefore, an additional measure such as batch extraction L3 to measure TDS release potential would still be recommended.

Table 2. Correlations between TDS and ABA parameters. MPA=Maximum Potential Acidity; SC=Specific conductance; r = correlation coefficient.

Rock Type	**N**	**Linear regression**	**Pearson Correlation**	
		SC_L3 = m*MPA + b	**r**	**P**
Leach 3				
Coal	3	SC_L3 = -89.6*MPA + 11700	-0.563	0.619
W. Refuse	14	SC_L3 = -7.74*MPA + 7280	-0.187	0.523
U. Refuse	17	SC_L3 = 75.6*MPA + 4010	0.835	<0.0001
Overburden	13	SC_L3 = 86.5*MPA + 1220	0.921	<0.0001
Shale	10	SC_L3 = 74.0*MPA + 2350	0.387	0.269
All data	58	SC_L3 = 57.9*MPA + 3350	0.663	<0.0001
Rock Type	**N**	**Linear regression**	**Pearson Correlation**	
		TDS_L3 = m*MPA + b	**r**	**P**
Coal	3	TDS_L3 = 56.8*MPA + 2170	0.989	0.0949
W. Refuse	14	TDS_L3 = -8.41*MPA + 8090	-0.167	0.568
U. Refuse	17	TDS_L3 = 130*MPA – 2770	0.858	<0.0001
Overburden	13	TDS_L3 = 196*MPA – 267	0.985	<0.0001
Shale	10	TDS_L3 = 26.1*MPA + 2420	0.326	0.358
All data	58	TDS_L3 = 100*MPA – 1880	0.692	<0.0001

Correlations between XRD-based mineral contents, ABA parameters, and selected leachate chemistry parameters (Supporting Information Table SI-11) confirmed that samples containing sulfide and sulfate minerals had higher total S, and samples containing calcite and dolomite had higher NP. The strongest predictor of leachate salinity (SC, TDS, or OP) was the total S content and the presence of sulfur minerals. These correlations support the hypothesis that Leach 1 liberates sulfur and iron mainly from iron sulfate minerals formed by prior oxidation of pyrite. Identification of iron sulfide minerals does not seem to be particularly informative for predicting water chemistry. Generally, the significance of correlations between ABA parameters and salinity parameters increases for Leach 3 (which seems to mobilize Ca from carbonates, whereas Leach 1 mobilizes Ca from gypsum).

3.6 Rock Type Fingerprinting

In certain situations, the ability to distinguish the source of TDS contamination is valuable. This becomes more challenging in the Appalachian Basin where coal mining, conventional oil and gas (O&G) production, and unconventional gas production all coexist. The ability to distinguish TDS inputs from coal versus O&G activities is important for establishing corrective and preventive actions. Bromide, strontium isotopes ($^{87}Sr/^{86}Sr$), and radium isotopes ($^{228}Ra/^{226}Ra$) have all been used to identify the addition of O&G produced water into freshwater systems (Chapman et al., 2012, Rowan et al., 2011, 2015; Jonson et al., 2015, Warner et al., 2012). As noted above, shales produced Na-Cl waters that were generally distinct from Ca-SO_4 waters produced from coal-associated rocks. Therefore, these potential geochemical tracers combined with chloride were examined for fingerprinting purposes.

Leachate chemistry from gas-producing shales (nine samples from Utica/Point Pleasant Shale plus one sample from Marcellus Shale) compared to coal mining-associated materials showed that differentiation with Cl versus Cl/SO_4 molar ratio and Cl versus $^{87}Sr/^{86}Sr$ isotope ratio are the most effective tools for source identification (Figure 8). Br was not a robust tracer in this study because it was below detection in most samples from coal-bearing strata (e.g., 24 of 65 samples had measurable Br in L1; 9 of 65 samples had measurable Br in L3). Where Br values were above detection limits, Cl/Br and Cl were greater in the gas-bearing shale samples compared to the coal-associated rocks. Ra isotopes were not effective tracers because of relatively large and overlapping variances in both total Ra activity and the $^{228}Ra/^{226}Ra$ isotope ratio for each rock type (Supporting Information Figure SI-3). $^{87}Sr/^{86}Sr$ isotope ratios

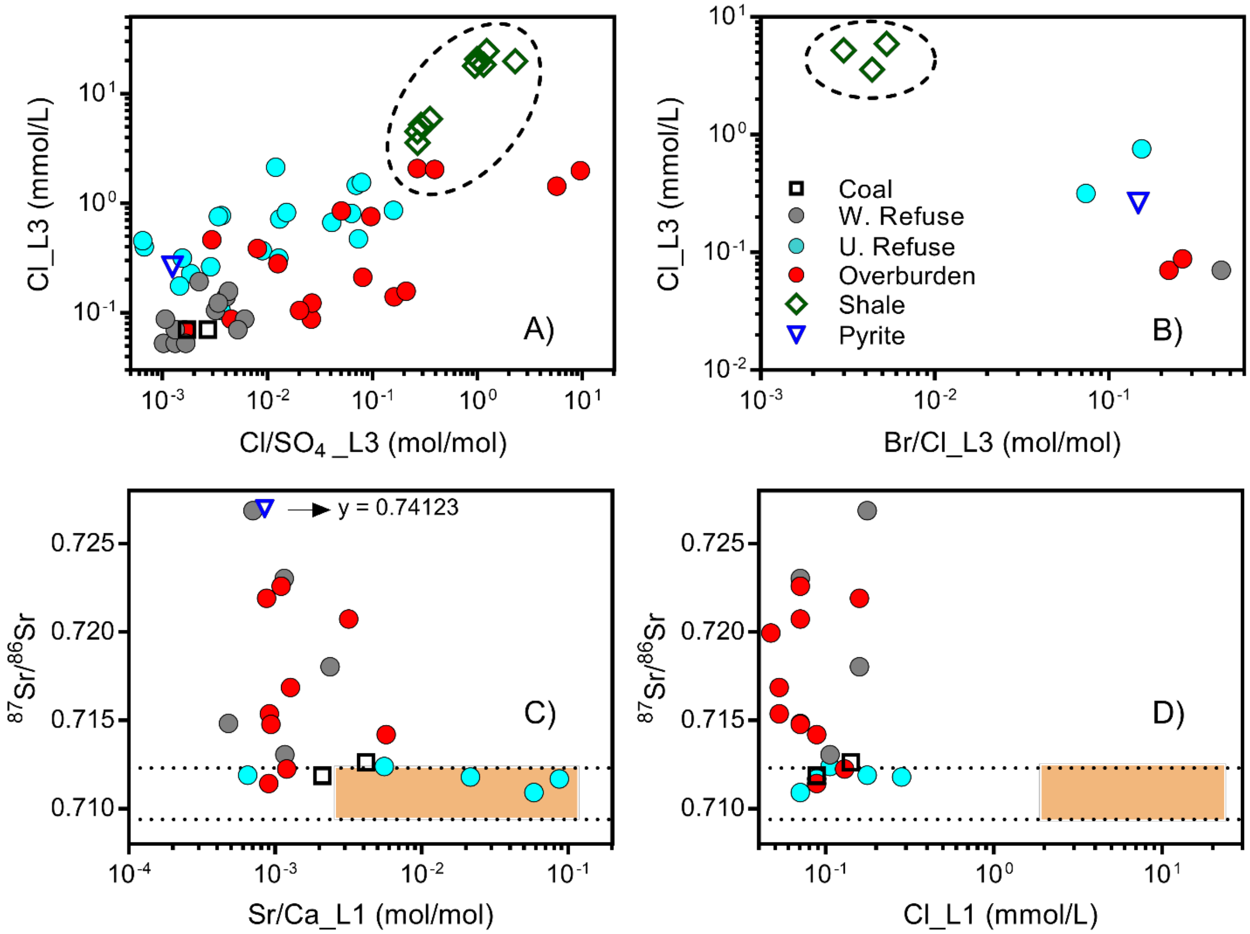


Figure 8. Potential geochemical relationships to distinguish leachates of gas-bearing black shales from coal-associated rocks. Dashed lines in C) and D) denote the 25th – 75th percentile values for $^{87}Sr/^{86}Sr$ ratios reported for Marcellus Shale and Utica/Point Pleasant Shale (Tasker et al., 2019). Shaded regions in C) and D) denote range of measured Sr/Ca ratios and Cl concentrations measured in the 10 gas-bearing shale samples analyzed in the current study paired with expected $^{87}Sr/^{86}Sr$ ratios from existing publications**.**

are effective because their range found in gas-producing shales is quite narrow and distinct from coal-associated formations. For example, the median $^{87}Sr/^{86}Sr$ isotope ratio for the Marcellus Shale compiled from over 133 samples is 0.7112 while the 25th to 75th percentiles range from 0.7110 to 0.7114 (Phan et al., 2016; Chapman et al., 2012; Capo et al., 2014; Blondes et al, 2017). The median $^{87}Sr/^{86}Sr$ isotope ratio for the Utica/Point Pleasant Shale from 26 samples is 0.7110 while the 25th to 75th percentiles range from 0.7109 to 0.7114 (Tasker et al., 2019). It must be noted that insufficient amounts of the shale samples used in this study were available for conducting $^{87}Sr/^{86}Sr$ isotope measurements. Instead, all gas-producing shale samples in Figure 8C,D are represented with the shaded region showing these 25th to 75th percentiles range. Using these well-constrained values for $^{87}Sr/^{86}Sr$ isotope ratios combined with Sr/Ca molar ratios or Cl concentrations, differentiation of TDS from gas-producing black shales and coal-associated rocks is possible.

4. CONCLUSIONS

Increased salinization of fresh water resources is a growing concern even in water-rich regions such as the Appalachian Basin. Management of activities and industries that release TDS could reduce this problem. For coal mining, segregation and isolation of rocks that produce high levels of TDS is one obvious management strategy. To implement this strategy, a rapid and simple method to identify these rocks by quantifying TDS release is required. In regions with coal mining and other sources of TDS (e.g., coal-bed methane, oil & gas development, road brining), source identification could also help reduce TDS release and enhance the information available to decision makers.

In this study, the mass of TDS released from sedimentary rocks (65 samples) was measured in laboratory batch extractions and compared to upscaled results from flow-through columns (19 samples) and field measurements (35 samples paired to 10 sites each with multiple field records). The pH of extractant blanks used for the batch tests decreased in the order DI (6.0), DI+CO_2 (5.1), and H_2O_2+CO_2 (2.6), which indicated the 30% H_2O_2 was mildly acidic as well as an oxidant. The DI extractant was effective for mobilizing soluble SO_4 and Cl salts, which are predominant sources of TDS upon initial wetting of crushed rock. The DI+CO_2 extractant increased the weathering of carbonates present in some samples, but did not significantly increase TDS production compared to the DI extraction when considering the whole set of samples. The H_2O_2+CO_2 extractant increased the weathering of sulfides (and carbonates) and resulted in the greatest TDS production and lowest pH values. When accounting for the mass of rock-to-volume of extractant, TDS measured in batch extractions was strongly correlated to cumulative TDS calculated from column experiments. TDS measured in batch extractions using 30% H_2O_2 under 10% CO_2 was higher and poorly correlated to cumulative TDS calculated from upscaled column experiments. Results suggest that the cumulative water-to-rock ratio controls leachate chemistry in batch extractions using DI water or flow-through configurations using synthetic rain.

Because all ions were not measured in field samples such that TDS concentrations could not be calculated, batch extractions and field measurements were compared based on SC. In contrast to column experiments, field SC was better correlated to SC measured from H_2O_2+CO_2 extractions versus DI extractions. The field SC and SC from H_2O_2+CO_2 extractions were statistically indistinguishable for 7 of 9 paired data sets while SC from DI extractions underestimated field SC in 5 of 9 cases. Compared to column leaching over months or waiting until mined rock begins weathering in the field, the batch extractions of small samples are efficient and informative. The small sample size used in batch tests permits testing of specific lithologies or strata. Results were comparable among the rapid batch tests and longer-term laboratory or field data sets. Upscaling comparisons suggest that (1) weathering reactions in the field are more aggressive than DI water or synthetic rainwater extractants used in batch or column tests, and (2) a batch extraction method utilizing 30% H_2O_2 (which is mildly acidic without CO_2 enrichment) could be effective for identifying rocks that will release high amounts of TDS.

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SUPPORTING INFORMATION

Batch Extraction Method to Estimate Total Dissolved Solids (TDS) Release from Coal Refuse and Overburden

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Eleven tables, three figures, and expanded version of materials and methods:

Supporting Information-1 – Expanded version of Materials and Methods

Sample Preparation

Samples were freeze-dried using a Labconco FreeZone 4.5 freeze dry system until constant weight was attained (~24 h). Samples were crushed to >4.75 mm using a hydraulic press at 44.5 kN of force and thereafter with a mortar and pestle until all particles were < 2 mm in diameter. Samples were further pulverized using a Spex 8000 ball mill to produce particles < 0.5 mm diameter (passed through No. 35 sieve).

Water Samples

Six water samples were collected from leachate drains of refuse piles at Mines A and B in March 2017. Conductivity and pH were measured in the field using a HACH HQ40 portable multimeter. Historical water quality data from these same leachate drains were compiled from Hydrologic Monitoring Reports (HMRs) submitted by the coal companies to the Pennsylvania Department of Environmental Protection (PA DEP). Historical water quality data from these same leachate drains were compiled from Hydrologic Monitoring Reports (HMRs) submitted by the coal companies to the Pennsylvania Department of Environmental Protection (PA DEP). HMR data spanned from 10/28/17 to 03/30/18 for Mine A, and from 10/07/14 to 10/26/17 for Mine B. Water samples were collected from the Skytop roadcut on May 2004.

Operational Extractions

Pulverized rock samples were sent to Geochemical Testing, a certified commercial laboratory in Somerset, PA, to conduct four operational extractions and analyze the various leachates. A fifth extraction was conducted at Pennsylvania State University to measure strontium isotopes ($^{87}Sr/^{86}Sr$). Extractions are summarized in Table SI-1.

Table SI-1. Summary of operational batch extractions and associated measurements.

Extraction Name	Extraction Conditions	Measured Analytes
Leach 1 (L1)	Deionized water in ambient atmosphere	SC, pH, TIC, major and trace metals, and anions
Leach 2 (L2)	Deionized water in 10/90% CO_2/N_2 atmosphere	SC, pH, TIC, major and trace metals, and anions
Leach 3 (L3)	30% H_2O_2 solution in 10/90% CO_2/N_2 atmosphere.	SC, pH, TIC, major and trace metals, and anions
Triple acid	Rock furnaced to ashes then digested in a solution of 70/30 HCl/HF and HNO_3.	Trace elements
Sr Leach (L4)	Deionized water in ambient atmosphere	Sr isotopes
Acid-base accounting	Pulverized solid samples	Neutralization potential (NP), total Sulfur

In Leach 1, rock samples were reacted with distilled deionized water (DI) under an ambient atmosphere. In Leach 2, rock samples were reacted with DI water under a 10/90% CO_2/N_2 atmosphere. In Leach 3, rock samples were reacted with a 30% H_2O_2 (70% DI) under a 10/90% CO_2/N_2 atmosphere. Aside from the differences noted above, the operational procedure for generating the three leaches followed the same steps. First, 10.00±0.05g of pulverized rock (<0.5-mm sieve size) was added to a 125 mL Erlenmeyer flask followed by 20.0 mL of the extraction solution. Addition of DI water in Leach 1 and Leach 2 was done rapidly in one aliquot. Addition of the H_2O_2 solution in Leach 3 was done slowly by adding 1.0 mL at a time to reduce effervescence of the reaction and loss of sample. The Erlenmeyer flasks were then placed on a shaker table inside a controlled atmosphere apparatus. The lid of the controlled atmosphere apparatus was left open for Leach 1 or sealed for Leach 2 and Leach 3. For the sealed conditions, 10% CO_2 and 90% N_2 gas was constantly flushed through the apparatus. All extractions were shaken for 4 hours at 50 rpm at room temperature. After the 4 hour reaction period, each sample was filtered through a 0.45-µm cellulose acetate filter and pH and specific conductance (SC) of the filtrate were measured immediately. The filtrate was transferred to a 100 mL volumetric flask and DI water was added to a final volume of 100 mL. This diluted sample was distributed into different containers for further analysis. Multiple blank samples were prepared with DI water or H_2O_2 and followed all steps described above.

Triple acid digestions were accomplished according to the standard method ASTM D 6357-11. Briefly, 2.5 g of pulverized rock (<0.5-mm) were ashed using a Thermolyne FA1740 furnace at 500 ^{0}C. Thereafter 0.5 g of ash was mixed with 20 mL of aqua-regia and 20 mL hydrofluoric acid in a beaker. The mixture was then heated to dryness followed by addition of 1 mL of concentrated nitric acid and 20 mL of DI water. After heating for 1 h at 100 ^{o}C and cooling to room temperature, the solution was diluted to 100 mL using DI water. The solution was then analyzed by inductively couple plasma mass spectrometer (ICP-MS) or inductively coupled plasma atomic emission spectroscopy (ICP-OES) following EPA methods 6010 and 6020 respectively.

Strontium leach (L4) was prepared by extracting the rock samples three times using DI water. First, 2.0 g of pulverized rock (<0.5-mm) and 15 mL of DI water were added into a 50 mL metal free plastic tube and shaken for 24 hours using a VWR Multi-tube Vortexer. Tubes were spun for 20 minutes at 3000 rpm using an Eppendorf 5810 R centrifuge and the supernatants were transferred to a new 50 mL tube. For the second extraction, 15 mL of DI water was added to the solid pellet, and the same steps described for the first extraction were followed. The same procedure was repeated for the third extraction with the exception that the tubes were shaken for 12 h. The three supernatants were combined and filtered (0.45-μm cellulose filter), preserved with nitric acid and kept at 4 ^{0}C until analyzed.

Analytical Methods

Table SI-2. Summary of analytical methods used for leachates.

Analytes	Method	Instrument[1]	Comments
SC	EPA 120.1	Conductivity meter	Measured in L1, L2, and L3
pH	SM 4500 H+B	pH meter	Measured in L1, L2, and L3
Major elements: Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si.	EPA 200.7	ICP-OES	Measured in L1, L2, and L3
Trace elements: Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Li, Lu, Mo, Nb, Nd, Ni, Pb, Rb, Sb, Se, Sm, Sn, Sr, Tb, Te, Th, Tl, Tm, Ti, U, V, W, Y, Yb, Zn, Zr	EPA 200.8 EPA 200.7	ICP-MS ICP-OES	Measured in L1, L2, and L3 B, Li and Ti were measured by ICP-OES. All other trace elements were measured by ICP-MS
Anions: Br, Cl, F, NO_3, NO_2, SO_4	EPA 300.0	IC	Measured in L1, L2, and L3
$^{87}Sr/^{86}Sr$	--	TIMS	Measured in L4

[1] IC=Ion chromatography; ICP-MS=Inductively couple plasma mass spectrometer; ICP-OES=Inductively coupled plasma atomic emission spectroscopy; TIMS=Thermal ionization mass spectrometry

Extracts from L1, L2, and L3 were filtered, and SC and pH were measured in the filtrate using an Oakton multiparameter PCTestr 35. Extracts were then diluted to 100 mL with DI water and the volume was split for the further analyses. TIC was measured following the ASTM D4839 method using an O.I Analytical 1010 TOC analyzer attached to an O.I. Analytical model 1051 autosampler. Hardness was calculated using mass concentration values of Ca and Mg (measured by ICP-OES).

Major and minor elements were meassured on a Thermo Scientific iCAP 7400 inductively coupled plasma optical emission spectrometer (ICP-OES), Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS), and Dionex DX-120 ion chromatography (IC) with AS22 and AG22 separation and guard columns (4 mm) at Geochemical Testing Lab (Somerset, PA).

Strontium from an aliquot of leach 4 (L4) containing approximately 100 to 800 ng of strontium was separated using Eichrom resin. Yield checks confirmed greater than 98% strontium recovery. $^{87}Sr/^{86}Sr$ was measured on a thermal ionization mass spectrometer (TIMS) located at the Penn State University Energy and Environmental Sustainability Laboratories. NIST SRM 987 and IAPSO seawater standards were also separated for strontium and analyzed concurrently with the samples to ensure data quality. The precision of the NIST standard during analysis was 0.7102599 ± 0.000009 (2 x Standard Error). To address any mass interference from ^{87}Rb after strontium separation, samples loaded onto filaments for the TIMS were heated past the ionization temperature of the Rb but below the ionization temperature of Sr. This removes some of the residual Rb in the samples. If ^{85}Rb is detected above its background concentration in the samples during analysis, the ^{87}Rb is estimated based on the natural abundance of ^{85}Rb and ^{87}Rb, and the $^{87}Sr/^{86}Sr$ ratio is calculated ($^{87}Sr = {}^{87}Total - {}^{87}Rb$). This correction was applied to 7 of the 23 analyzed samples.

Table SI-3. Summary of analytical methods used for solids.

Analytes	Method	Instrument
Acid-Base Accounting parameters: NP	Sobek	Titration equipment
Total Sulfur (%)	ASTM D4239-17	Furnace
Triple acid digestion: Al, Fe, Mn, Ca, Mg, Na, K, Si, P, S, Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Li, Lu, Mo, Nb, Nd, Ni, Pb, Rb, Sb, Se, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr	ASTM D5367-11 EPA 6010 EPA6020	Furnace ICP-AES ICP-MS
226/228Ra		Gamma spectrometer
X-ray diffraction (XRD)		X-Ray Diffractometer

Neutralization potential (NP) was determined as the amount of acid neutralized by the sample in $CaCO_3$ equivalents expressed as g/kg (Mg /1000 Mg of rock). Total sulfur (%) was analyzed using a LECO 628 analyzer equipped with sulfur add-on module, following the directions of the ASTM D4239-

17 method. Maximum potential acidity (MPA) was calculated from the sulfur content assuming complete oxidation of pyrite and neutralization of all generated acidity, according to the following reaction[2]:

$$FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O \Leftrightarrow Fe(OH)_3 + 2SO_4^{-2} + 2Ca^{+2} + 2CO_2 \qquad \text{Eq SI-1}$$

Therefore, after stoichiometry equivalences, MPA was calculated as:

$$MPA\ \left(g\,\frac{CaCO_3}{kg}\right) = S\ (\%) * 31.25 \qquad \text{Eq SI-2}$$

where *S* is the total sulfur concentration (weight percent), and 31.25 is a stoichiometric conversion factor based on Eq SI-1. Net neutralization potential (NNP) in units of (g $CaCO_3$/kg) was calculated by subtracting MPA from NP. The MPA computation (and that for NNP) assumes the acidity produced from 1 mol FeS_2 (64 g of S) is neutralized by 2 mol $CaCO_3$ (200 g) (Cravotta et al., 1990). On this basis, 31.25 g of $CaCO_3$ will neutralize the acidity from 1,000 g of rock that contains 1.0 weight percent (%) pyritic sulfur.

Radium isotopes (^{226}Ra, ^{228}Ra) were measured using a small anode germanium detector gamma spectrometer from Canberra Instruments at geometries consistent with internal standards and certified reference materials (UTS-2). After a 21 day equilibration, ^{226}Ra was calculated from the average activity of Bi-214 (609 keV) and Pb-214 (295 & 351 keV). Direct measurement of ^{228}Ra was performed using its ^{228}Ac daughter at 911.16 keV.

Sediment mineralogy was characterized by qualitative X-ray diffraction (XRD) using a PANanalytical X'Pert 165 PRO MPD located in the Materials Characterization Lab at Pennsylvania State University. The X-ray diffractometer ran from 5-70 degrees 2-theta at a power setting of 45 kV and 40 mA, with a PIXcel detector that was operated in line scanning mode with an active length of 3.34 degrees. Incident side set-up consisted of a 1/4 degree divergence slit and a 1/2 degree anti-scatter slit, and 0.04 radians Soller slits. The diffracted side utilized a 1/4 degree receiving slit, 0.04 radian Soller slits, and a Ni filter. The collected data were then analyzed using JADE for phase identification.

Speciation Modeling Methods

The PHREEQC 3.0 aqueous speciation model (Parkhurst and Appelo, 2013) was used with input values for effluent data to estimate SC by methods reported by Appelo et al. (2013) and McCleskey et al. (2012). Input data to PHREEQC included the sample temperature, pH, and the mass concentrations (mg/L) of total inorganic carbon (TIC), SO_4, Cl, F, Br, NO_3-N, P, Si, Ca, Mg, Na, K, Li, Fe, Mn, Al, Ba, Sr, and Zn in the effluent after filtration (< 0.45 μm pore size). Both methods calculate SC using the same speciated cations and anions (H^+, Li^+, Na^+, K^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, F^-, Cl^-, Br^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_3^- , and OH^-), trace metals (Al^{3+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, and Zn^{2+}), and charged ion pairs (HSO_4^-, $NaSO_4^-$, $NaCO_3^-$, and KSO_4^-). However, the computations used to determine ionic conductivities are different.

Briefly, the Appelo et al. (2013) method calculates the ionic conductivity ($\lambda_{0,i}$) of the above solute species using diffusion coefficient (Dw), ionic charge (z), Faraday's constant (F), gas constant (R), and absolute temperature (T) (equation SI-3)

$$\lambda_{0.i} = \frac{z^2 F^2}{RT} D_w \qquad \text{Eq SI-3}$$

Then, conductance (κ) at sample temperature is calculated as the sum of the individual ionic conductivities multiplied by the speciated concentration (m) and the activity coefficient (γ_{sc}) using equation SI-4:

$$\kappa = \sum(\lambda_{0,i}\gamma_{sc}m_i) \qquad \text{Eq SI-4}$$

The McCleskey at al. (2012) method calculates ionic molal conductivities (λ_i) at sample temperature (T) and ionic strength (I) using equation SI-5.

$$\lambda_i = \lambda^0(T) - \frac{A(T)I^{0.5}}{1+BI^{0.5}} \qquad \text{Eq SI-5}$$

where I is calculated as equation SI-6

$$I = 0.5 \sum m_i \, {z_i}^{0.5} \qquad \text{Eq SI-6}$$

For the above equations, i is the ion and z is its charge, and λ^0 and A are functions of temperature and B is an empirical constant. McCleskey et al. (2012) then compute the conductance at sample temperature as the sum of the products of molal ionic conductivity (λ_i) and the molal concentration of each of the species (m_i) (equation SI-7)

$$\kappa = \sum \lambda_i m_i \quad \text{Eq SI-7}$$

Individual contributions to the SC, expressed as the transport number (t), were calculated from the conductivity determined by McCleskey at al. (2012) method using equation SI-8

$$t_i = \frac{\lambda_i m_i}{\kappa} \quad \text{Eq SI-8}$$

Both of the above-cited methods indicate the computed conductance at the sample temperature. Because the temperature in the laboratory was 25 ºC, the computed conductance for each sample equals its specific conductance at 25 ºC (SC). For conductivity estimates at other temperatures, the SC can be calculated assuming the conductivity changes approximately 2.1 percent per degree C as reported by McCleskey at al. (2012) (equation SI-9):

$$\mathrm{SC} = \frac{\kappa(T)}{1+0.021\,(\mathrm{T}-25)} \quad \text{Eq SI-9}$$

The data used as input to, or computed as output from, PHREEQC 3.0 were also used to compute total dissolved solids (TDS) and osmotic pressure (OP). The TDS was computed as the sum of the input concentrations of major dissolved constituents (Ca, Mg, Na, K, SO_4, Cl, CO_3, NO_3, SiO_2) (Fishman and Friedman, 1989, p. 437-438) plus minor constituents (Sr, Ba, Fe, Al, Mn, Br), in mg/L, assuming that Fe, Al, and Mn formed hydrous oxides (FeOOH, AlOOH, MnOOH) instead of anhydrous compounds. Cravotta and Brady (2015) showed that TDS computed accordingly was comparable to the laboratory measured residue on evaporation at 180 ºC for mine effluent samples.

Osmotic pressure (OP) was computed as the sum of molal concentrations of the same aqueous species used for conductivity calculation. The OP computation assumes that 1 mol/kg of each ion exerts approximately 1 mOsm/kg osmotic pressure (Haynes et al., 2013). Cravotta and Brady (2015) showed that the OP computed accordingly was comparable to the laboratory measured OP for mine effluent samples. Measured OP normally is determined using freezing point depression, by which an Osmol is defined as the number of moles of a solute required to lower the freezing point of 1 kg of water by 1.858^{0}C (Kiyosawa, 2003).

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Statistical Methods

One of the goals of our study was to compare the different leaching methods. For this evaluation, we first identified outliers by comparing results of SC measured in the extraction leaches with their corresponding SC calculated by McCleskey method[19] (results not shown). Thereafter, statistical differences between leachates for selected parameters (SC, TDS, and pH) were evaluated using the Wilcoxon signed-rank test. SC and TDS were compared via correlation (Pearson) analyses. In addition, linear regression equations were generated for each rock category and for the full data set. The next goal of our study was to compare our batch extractions with column studies and field data. Comparisons between TDS from leaches against TDS data derived from column experiments were made using the Pearson correlation and by comparing the fit of our data (R^2) with line Y = X. Finally, SC data from the field was compared with SC results of our leaches using antwo sample t-test.

Table SI-7. Summary of statistical comparisons (Wilcoxon signed-rank test) between selected properties (measured or calculated) in the three batch extractions. SC_L - Specific conductance measured in leachates; SC_CM – Specific conductance calculated by McCleskey method; TDS – Total dissolved solids (calculated); Sig. Diff. – Significantly different in a 95% confidence interval.

Comparison	**SC_L**		**SC_CM**		**TDS**		**pH**	
	P value	**Sig. Diff.**	**P value**	**Sig. Diff.**	**P value**	**Sig. Diff.**	**P value**	**Sig. Diff.**
L1 vs L2	0.3477	N	0.7987	N	0.0715	N	0.8077	N
L1 vs L3	<0.0001	Y	<0.0001	Y	<0.0001	Y	<0.0001	Y
L2 vs L3	<0.0001	Y	<0.0001	Y	<0.0001	Y	<0.0001	Y

Table SI-8. Correlations between TDS from column experiments and TDS from batch extractions. TDS=Total dissolved solids; r = correlation coefficient; R^2 = regression coefficient.

Comparison	Pearson Correlation		Linear Regression	Linear Regression
	r	P	TDS_Columns = m*TDS_L1 + b	Y=X
TDS_Column vs TDS_L1	0.989	<0.0001	Y = 1.09*X + 0.182	R^2 = 0.9594
TDS_Column vs TDS_L3	0.922	<0.0001	Y = 0.255*X + 0.597	R^2 = -9.150

Table SI-9. Summary of statistical comparisons (Unpaired t-test) between specific conductance measured in batch extractions and corresponding field sites. SC_L1 - Specific conductance measured in Leach 1; SC_L3 - Specific conductance measured in Leach 3; Sig. Diff. – Significantly different at a 95% confidence interval.

Field Site	Comparison			
	SC_L1		SC_L3	
	P value	Sig. Diff.	P value	Sig. Diff.
Mine A	<0.0001	Y	0.0856	N
Mine B	<0.0001	Y	0.9142	N
Mines P	0.2917	N	0.8079	N
KY1	0.0466	Y	0.475	N
KY2	0.0009	Y	0.6466	N
KY3	0.0826	N	0.004	Y
KY9	n.d.	n.d.	n.d.	n.d.
LKFC	0.0853	N	<0.0001	Y
BCS3	0.7255	N	0.094	N
Skytop	0.0007	Y	0.0538	N

n.d. – not determined because of insufficient data

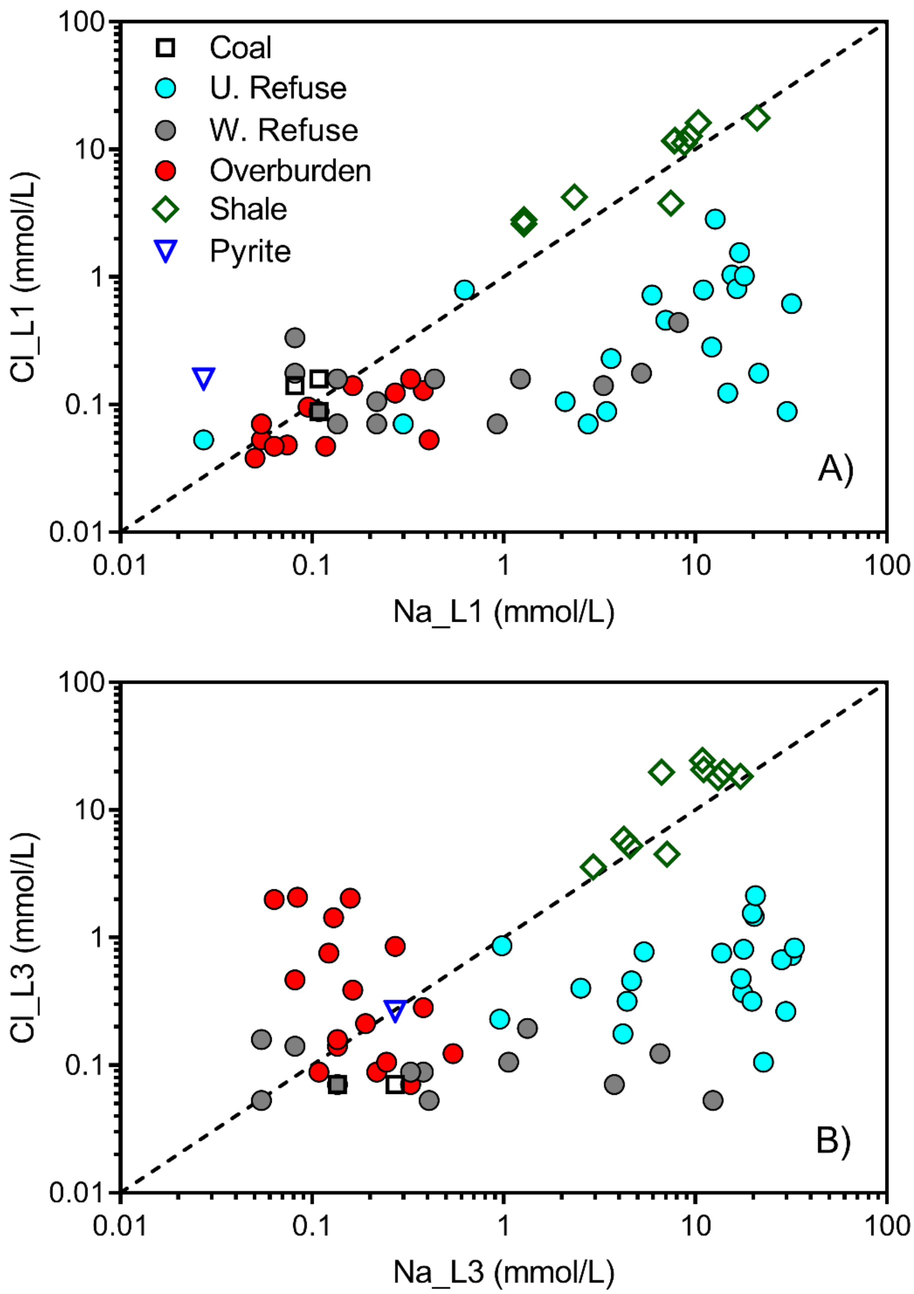

Figure SI-1. Plots of Cl versus Na molar concentrations in both L1 and L3 as compared to 1:1 line of equality.

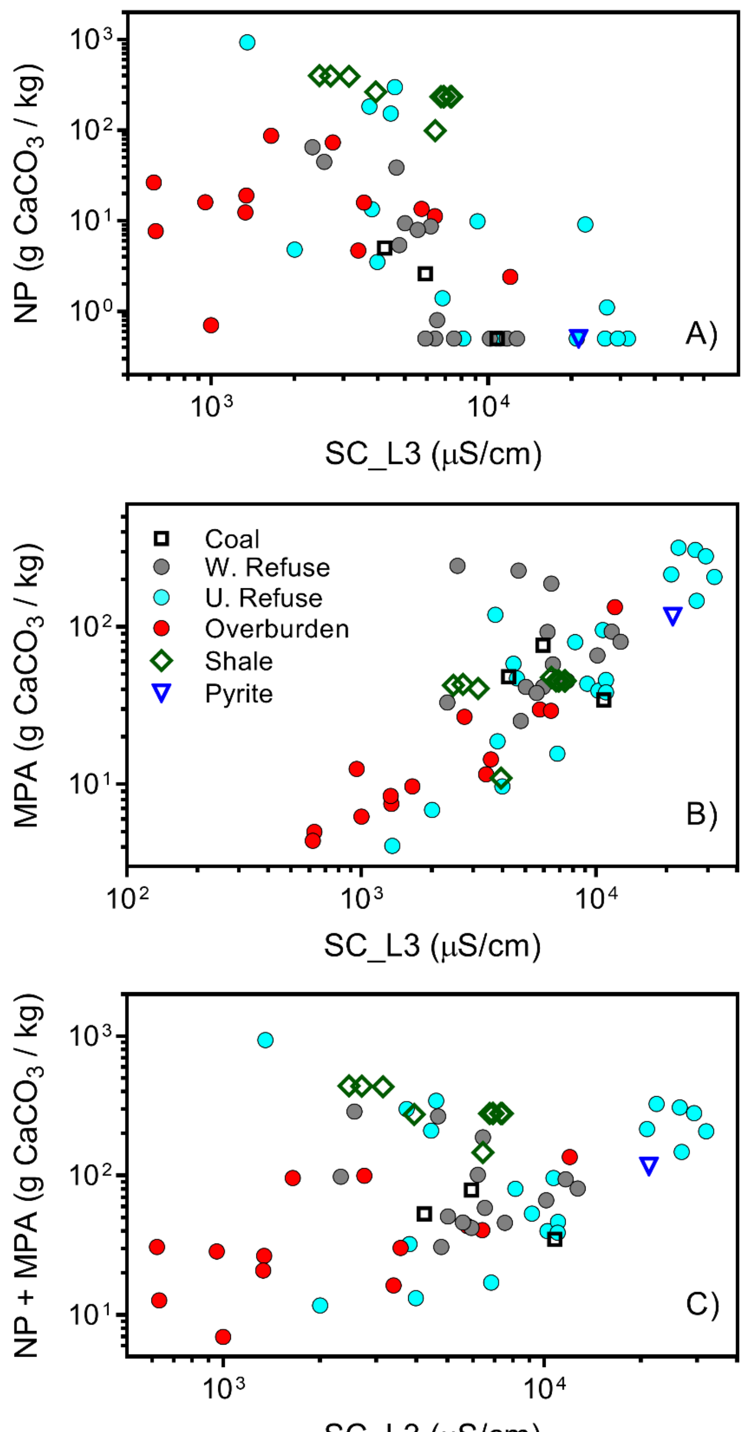

Figure SI-2. Relationships between specific conductance (SC) in leach 3 (H_2O_2+CO_2) and acid base accounting (ABA) parameters.

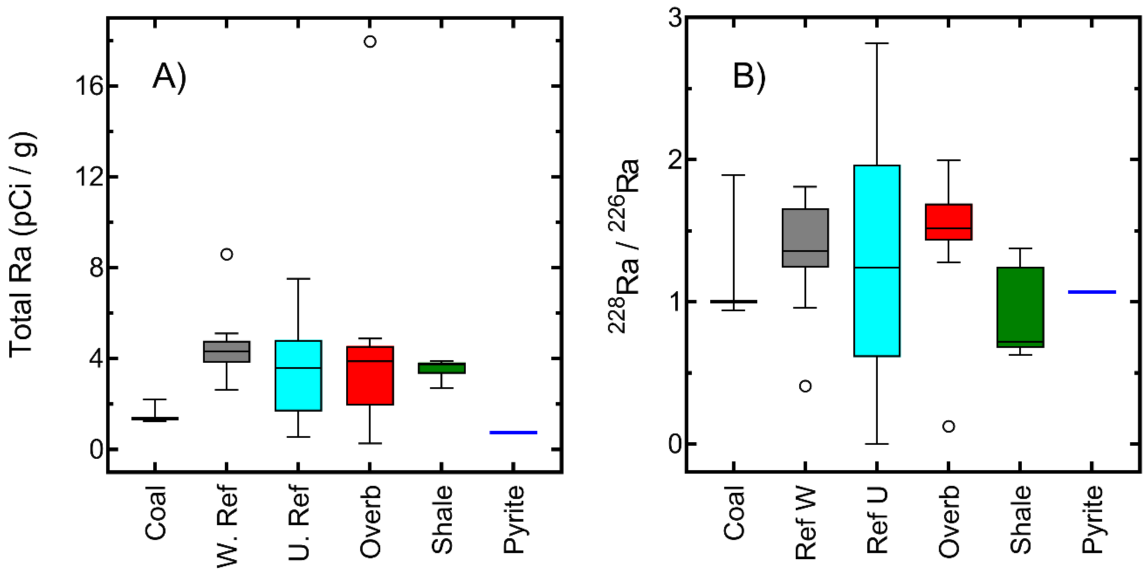

Figure SI-3. Total Ra and $^{228}Ra/^{226}Ra$ isotope ratios for the six rock types. Coal (n=3); Weathered Coal Refuse = W. Ref (n=14); Unleached Coal Refuse = U. Ref (n=20); Overburden = Overb (n=17); Shale (n=10); Pyrite (n=1). Box plots show median, 25% and 75% quartile ranges.

Table SI-4. Sample descriptions and associated PHREEQC input and output data for rapid leach samples: typ
[element concentrations corrected for dilution of initial leach volume to 100 ml; concentration values origi

ROCKTYPE Class	MASS g	VOL ml	SAMPLE Name	LEACH Type	TEMPC C	pe	pH	TIC mg/L
Coal	9.96	20	PA1	001	25	4	6.8	5.4
Coal	9.99	20	PA1	002	25	4	6	27.3
Coal	9.96	20	PA1	003	25	4	2.3	4
Coal	10	20	PA45	001	25	4	2.8	3.4
Coal	9.97	20	PA45	002	25	4	2.9	9.7
Coal	10.03	20	PA45	003	25	4	1.6	14.9
Coal	9.96	20	PA5	001	25	4	4.7	3.1
Coal	9.98	20	PA5	002	25	4	6	18.9
Coal	9.98	20	PA5	003	25	4	2	6.1
Overburden	9.97	20	BCS3	001	25	4	7.5	14.1
Overburden	9.99	20	BCS3	002	25	4	7.1	49.3
Overburden	10	20	BCS3	003	25	4	6.7	39.5
Overburden	9.96	20	HCS	001	25	4	3.6	9
Overburden	9.99	20	HCS	002	25	4	3.4	14.3
Overburden	9.97	20	HCS	003	25	4	1.5	29.8
Overburden	10.05	20	KBFWV	001	25	4	7.4	19.9
Overburden	10.04	20	KBFWV	002	25	4	7	93.8
Overburden	10.02	20	KBFWV	003	25	4	7.3	74.4
Overburden	10.01	20	KY1	001	25	4	6.9	5.7
Overburden	10.01	20	KY1	003	25	4	3.4	4.6
Overburden	9.99	20	KY2	001	25	4	7.7	5.6
Overburden	9.99	20	KY2	003	25	4	7	13
Overburden	10.01	20	KY3	001	25	4	7.2	5.4
Overburden	10.01	20	KY3	003	25	4	6.5	6.4
Overburden	9.99	20	KY4	001	25	4	7	6
Overburden	9.99	20	KY4	003	25	4	4.1	21.7
Overburden	10.01	20	KY7	001	25	4	6.2	5.7
Overburden	10.05	20	KY7	002	25	4	6.4	14.6
Overburden	10.02	20	KY7	003	25	4	2.4	16.3
Overburden	10.01	20	KY9	001	25	4	6.9	5.3
Overburden	10	20	KY9	002	25	4	5.8	31.6
Overburden	10.05	20	KY9	003	25	4	2.7	7.3
Overburden	9.99	20	LKFC	001	25	4	5	1.8
Overburden	10	20	LKFC	002	25	4	5.1	5.3
Overburden	10.01	20	LKFC	003	25	4	2.1	9.8
Overburden	9.99	20	MKSS	001	25	4	6.8	10
Overburden	10	20	MKSS	002	25	4	7.4	56.9
Overburden	10.01	20	MKSS	003	25	4	6.8	65.4
Overburden	9.96	20	TN2	001	25	4	6.8	16.8
Overburden	10.04	20	TN2	002	25	4	7.6	72.5
Overburden	9.99	20	TN2	003	25	4	6.9	56.6
Refuse	9.98	20	PA12	001	25	4	3.7	3.1

Table SI-5. Sample descriptions and associated PHREEQC input and output data for blank samples: type 1 (c
[element concentrations corrected for dilution of initial leach volume to 100 ml; concentration values origi

ROCKTYPE	MASS	VOL	SAMPLE	LEACH	TEMPC	pe	pH	TIC
Class	g	ml	Name	Type	C			mg/L
n.a.	0	20	Blank	001	25	4	6	1.4
n.a.	0	20	Blank1	001	25	4	4.8	3.8
n.a.	0	20	Blank2	001	25	4	5.7	4
n.a.	0	20	Blank3	001	25	4	6.8	3.9
n.a.	0	20	Blank4	001	25	4	7	45.4
n.a.	0	20	Blank5	001	25	4	4.1	8.3
n.a.	0	20	Blank6	001	25	4	7	5.8
			Median				6.0	
			Min				4.1	
			Max				7.0	
n.a.	0	20	Blank	002	25	4	5.1	5.8
n.a.	0	20	Blank1	002	25	4	4.4	14.7
n.a.	0	20	Blank2	002	25	4	4.8	6.1
n.a.	0	20	Blank3	002	25	4	5.8	15.4
n.a.	0	20	Blank4	002	25	4	6.3	35.2
			Median				5.1	
			Min				4.4	
			Max				6.3	
n.a.	0	20	Blank	003	25	4	2	6.1
n.a.	0	20	Blank1	003	25	4	3.6	4.3
n.a.	0	20	Blank2	003	25	4	2.6	10
n.a.	0	20	Blank3	003	25	4	2.7	12.5
n.a.	0	20	Blank4	003	25	4	4.5	8.8
n.a.	0	20	Blank5	003	25	4	2.2	4.8
n.a.	0	20	Blank6	003	25	4	1.8	5.1
			Median				2.6	
			Min				1.8	
			Max				4.5	

Table SI-6. Chemical composition of rock samples used for rapid leach tests.
[elemental analysis conducted on ashed samples digested in HCl+HNO3 (partial digestion); MPA, maxi

SAMPLE	LEACH	ROCKTYPE2	MPA g/kg	NP g/kg	NNP g/kg	STOT mg/kg	Fe mg/kg	Mn mg/kg
PA1	004	coal	48.1	0.5	-47.6	15400	13000	21
PA45	004	coal	34.4	<0.05	-34.35	11000	8720	14.5
PA5	004	coal	76.2	0.26	-75.94	24400	20600	21.9
BCS3	004	overburden	26.9	7.29	-19.61	8600	77300	1220
HCS	004	overburden	134	0.24	-133.76	42800	53900	317
KBFWV	004	overburden	12.5	1.6	-10.9	4000	54800	874
KY1	004	overburden	<0.31	0.17	-0.14	<100	19.9	147
KY2	004	overburden	<0.31	3.51	3.2	<100	14.3	322
KY3	004	overburden	<0.31	1.88	1.57	<100	26	417
KY4	004	overburden	0.31	0.43	0.12	100	53.2	350
KY7	004	overburden	29.4	1.12	-28.28	9400	52300	958
KY9	004	overburden	11.6	0.47	-11.13	3700	16800	287
LKFC	004	overburden	29.9	1.36	-28.54	9570	69100	1350
MKSS	004	overburden	9.69	8.66	-1.03	3100	25200	553
TN2	004	overburden	7.5	1.9	-5.6	2400	30100	401
VA16	004	overburden	5	0.77	-4.23	1600	14900	380
VA2	004	overburden	14.4	1.59	-12.81	4600	42700	675
VA3	004	overburden	6.25	0.07	-6.18	2000	32700	287
VA6	004	overburden	8.44	1.24	-7.2	2700	53500	653
WV5	004	overburden	4.38	2.64	-1.74	1400	25200	493
PA12	004	refuse	57.8	0.08	-57.72	18500	43500	169
PA13	004	refuse	65.9	<0.05	-65.85	21100	32700	139
PA17	004	refuse	188	<0.05	-187.95	60200	65700	36.8
PA22	004	refuse	228	3.86	-224.14	73000	84000	153
PA30	004	refuse	244	4.48	-239.52	78100	89500	172
PA31	004	refuse	92.8	0.87	-91.93	29700	48100	275
PA36	004	refuse	93.4	<0.05	-93.35	29900	53700	185
PA42	004	refuse	41.6	0.94	-40.66	13300	34000	195
PA48	004	refuse	80.3	<0.05	-80.25	25700	42800	160
PA51	004	refuse	41.6	<0.05	-41.55	13300	46600	105
PA58	004	refuse	45.3	<0.05	-45.25	14500	41600	147
TNR1	004	refuse	25.3	0.54	-24.76	8100	32100	189
TNR2	004	refuse	33.1	6.49	-26.61	10600	31400	171
TNR3	004	refuse	38.1	0.79	-37.31	12200	38400	246
TGS1	004	refuseU	43.4	0.99	-42.41	13900	32000	175
TGS10A	004	refuseU	208	<0.05	-207.95	66400	98500	41.6
TGS10B	004	refuseU	45.9	<0.05	-45.85	14700	27900	71.9
TGS11	004	refuseU	6.88	0.48	-6.4	2200	10600	31.3
TGS12	004	refuseU	280	<0.05	-279.95	89600	122000	264
TGS13	004	refuseU	4.06	93.5	89.44	1300	3940	1790
TGS14	004	refuseU	216	<0.05	-215.95	69000	97200	212
TGS15	004	refuseU	38.4	<0.05	-38.35	12300	21100	67.1
TGS17	004	refuseU	58.4	15.2	-43.2	18700	31800	318

Table SI-10. Summary of field chemistry and leachate results for the 10 paired field sites.
L1 (deionized water), and L3 (30% H2O2+10% CO2).

Analyte		MA_F	MA_L1	MA_L3	MB_F	MB_L1	MB_L3	SK_F	SK_L1	SK_L3	MP_F	MP_L1
SC	Mean	8,110	2,350	6,060	8,240	2,180	8,170	21,100	5,480	25,900	11,400	6,270
µS/cm	Max	13,500	3,180	10,100	14,000	2,880	12,700	30,300	7,140	28,500	13,000	31,100
	Min	3,820	1,640	2,100	2,520	1,190	5,010	11,700	4,060	21,200	9,690	340
pH	Mean	3.6	4.1	2.3	3.6	4.4	2.1	2.2	2.8	1.3	6.8	4.6
	Max	5.8	6.2	3.3	7.2	6.8	2.5	2.3	2.9	1.5	7.6	7.6
	Min	2.5	2.6	1.8	2.7	2.9	1.7	2.0	2.7	1.2	6.3	2.2
Ca	Mean	NP	364	401	NP	295	463	NP	56.3	248.1	0.32	136
mg/L	Max	NP	446	501	NP	410	526	NP	56.3	248.1	0.41	491
	Min	NP	234	121	NP	42.5	398	NP	56.3	248.1	0.15	1.88
Mg	Mean	NP	30.1	67.9	NP	72.5	111	NP	27.5	36.3	168	58.6
mg/L	Max	NP	55.6	99.4	NP	144	197	NP	27.5	36.3	242	230
	Min	NP	15.0	16.9	NP	3.75	53.8	NP	27.5	36.3	35.0	0.313
Na	Mean	NP	3.50	4.50	NP	51.0	82.1	NP	0.625	6.250	2,270	275
mg/L	Max	NP	5.00	9.38	NP	188	284	NP	0.625	6.250	2,660	731
	Min	NP	1.88	1.25	NP	1.88	1.25	NP	0.625	6.250	2,030	6.88
K	Mean	NP	2.88	2.88	NP	4.69	9.27	NP	1.88	12.50	25.9	12.4
mg/L	Max	NP	5.00	6.88	NP	12.5	35.0	NP	1.88	12.50	54.6	29.2
	Min	NP	1.25	1.25	NP	1.25	1.25	NP	1.88	12.50	11.2	1.25
Fe	Mean	969	190	971	1,160	49.3	1,390	9,525	863	5860	352	3,260
mg/L	Max	2,180	788	1,690	3,470	119	2,590	18,200	863	5860	590	32,300
	Min	20.9	5.25	66.3	11.4	0.125	466	1,850	863	5860	2.26	0.125
Al	Mean	43.1	32.0	69.9	168	36.3	164	3,670	535	781	0.721	201
mg/L	Max	117	80.6	162	511	77.5	251	6,430	535	781	2.03	1,300
	Min	4.37	0.313	3.13	3.21	0.313	47.5	1,190	535	781	0.033	0.313
Mn	Mean	20.0	4.80	12.5	40.6	9.07	19.9	234	0.438	0.750	5.13	2.76
mg/L	Max	53.3	11.3	22.1	64.0	20.5	31.9	444	0.438	0.750	9.67	10.50
	Min	6.37	1.63	1.06	3.14	0.044	7.38	44.0	0.438	0.750	0.590	0.013
SO_4	Mean	5,040	1,220	2,680	8,450	1,230	4,130	57,300	2,850	17,100	4,920	4,890
mg/L	Max	9,840	1,870	4,310	26,300	1,730	6,690	97,600	2,850	17,100	8,130	52,400
	Min	1,820	675	969	1,670	488	1,960	20,900	2,850	17,100	1,860	3.13
HCO_3	Mean	NP	2.27	0.006	NP	19.8	0.003	NP	0.007	0.001	NP	31.0
mg/L	Max	NP	9.81	0.022	NP	82.3	0.006	NP	0.007	0.001	NP	228
	Min	NP	0.003	0.001	NP	0.007	0.002	NP	0.007	0.001	NP	0.003
Cl	Mean	NP	5.38	2.63	NP	7.63	4.00	NP	5.63	9.38	1,370	22.2
mg/L	Max	NP	11.9	5.00	NP	15.6	6.88	NP	5.63	9.38	2,020	101
	Min	NP	2.50	1.25	NP	5.00	1.88	NP	5.63	9.38	397	2.50

Field site	Rock samples	Field measureme
Mine A	Weathered refuse n=5	Field sampling + I
Mine B	Weathered refuse n=6	Field sampling + I
Mines P	Unweathered refuse n=17	Field sampling n=
KY1	Weathered overburden n=1	Automated SC m

Table SI-11. Spearman rank correlation coefficient (r) matrix for XRD, acid-base account parame
[r-values multiplied by 100 and rounded; only values significant at α = 0.001 shown]

LEACH001+002+003	1 NPppt	2 MPAppt	3 NNPppt	4 MPANPppt	5 FeSulfide	6 FeSulfate	7 Gypsum	8 Carbonate	9 Sminl	10 CO3Sminl	11 SC25lab	12 KScalc	13 SC25phrq	14 TDSphrq	15 OSMPphrqm
1 NPppt	100	-32	54			-50		74		37	-40	-26	-40	-48	-28
2 MPAppt	-32	100	-92	91	63	32			71	47	62	44	62	66	59
3 NNPppt	54	-92	100	-75	-42	-35	-27	27	-58		-62	-47	-62	-69	-55
4 MPANPppt		91	-75	100	67				66	56	54	42	55	57	55
5 FeSulfide		63	-42	67	100			32	61	62					28
6 FeSulfate	-50	32	-35			100		-29	40		39		38	41	32
7 Gypsum			-27				100		37						
8 Carbonate	74		27		32	-29		100		74				-25	
9 Sminl		71	-58	66	61	40	37		100	75	46		46	48	42
10 CO3Sminl	37	47		56	62			74	75	100					
11 SC25lab	-40	62	-62	54		39			46		100	78	98	97	97
12 KScalc	-26	44	-47	42							78	100	78	75	77
13 SC25phrq	-40	62	-62	55		38			46		98	78	100	98	97
14 TDSphrq	-48	66	-69	57		41		-25	48		97	75	98	100	93
15 OSMPphrq	-28	59	-55	55	28	32			42		97	77	97	93	100
16 pH	76	-46	61	-33		-43		59	-32		-65	-56	-70	-74	-57
17 TIC	58	-29	44					48						-30	
18 ALK	79	-45	61	-29		-45		62	-32		-63	-52	-65	-70	-53
19 NALK	71	-54	66	-44		-48		49	-39		-72	-53	-76	-82	-64
20 NACID	-71	54	-66	44		48		-49	39		72	53	76	82	64
21 SO4	-54	63	-70	52		42		-33	42		94	72	94	98	88
22 Fe	-68	54	-65	46		47		-51	35		65	49	69	75	60
23 Ca		41	-34	43			41		46	44	61	48	62	63	57
24 Mg	-29	25	-36				33				63	46	62	67	54

LEACH001	1 NPppt	2 MPAppt	3 NNPppt	4 MPANPppt	5 FeSulfide	6 FeSulfate	7 Gypsum	8 Carbonate	9 Sminl	10 CO3Sminl	11 SC25lab	12 KScalc	13 SC25phrq	14 TDSphrq	15 OSMPphrqm
1 NPppt	100		54			-50		76		43	-45		-44	-54	
2 MPAppt		100	-91	91	61				71	44	71	56	73	74	67
3 NNPppt	54	-91	100	-75					-55		-74	-58	-75	-80	-64
4 MPANPppt		91	-75	100	67				65	54	60	52	63	62	61
5 FeSulfide		61		67	100				62	64					
6 FeSulfate	-50					100					45		46	46	
7 Gypsum							100								
8 Carbonate	76							100		77					
9 Sminl		71	-55	65	62				100	74	49		54	51	49

Table SI-4. Sample descriptions and associated PHREEQC input and output data for rapid leach samples: type 1 (deionized water), type 2 (10% CO2), and type 3 (30% H2O2+10% CO2).

[element concentrations corrected for dilution of initial leach volume to 100 ml; concentration values originally reported as less than detection limit shown equal to the detection limit; nd, no data]

SORT1 SORT2
1 1

ROCKTYPE	MASS	VOL	SAMPLE	LEACH	TEMPC	pe	pH	TIC	SO4	Cl	F	Br	NO3N	P	Si	Ca	Mg	Na	K	Li	Fe	Mn	Al	Ba	Sr	Zn	Co	Se	Sp. Conduct., µS/cm at 25 °C			TDS	OSMP	IonStr	2	2
Class	g	ml	Name	Type	C			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	Measured	McCleskey	PHREEQC	mg/L	mOsm/kg	mol/L	3	3
Coal	9.96	20	PA1	001	25	4	6.8	5.4	244	5.63	0.31	0.63	0.31	0.03	5.63	96.9	2.5	2.5	3.75	0.03	5.5	0.25	0.313	0.131	0.252	0.033	0.192	0.013	576	548	556	375	5.11	0.009	50	4
Coal	9.99	20	PA1	002	25	4	6	27.3	328	3.75	0.31	0.63	0.38	0.03	3.75	110	2.5	3.75	1.25	0.03	74.4	0.375	0.313	0.108	0.316	0.109	0.371	0.013	710	729	750	600	7.25	0.013	51	5
Coal	9.96	20	PA1	003	25	4	2.3	4	2920	1.25	0.31	0.63	0.31	0.5	8.75	490	15.6	2.5	3.75	0.03	631	2.75	7.5	0.056	0.975	0.963	0.963	0.436	4230	5180	5530	4700	43.30	0.071	52	6
Coal	10	20	PA45	001	25	4	2.8	3.4	561	3.13	0.31	0.63	0.25	0.13	12.5	63.1	12.5	2.5	1.25	0.06	78.8	1.12	21.2	0.124	0.289	0.481	0.211	0.066	1430	1420	1450	873	9.36	0.016	80	7
Coal	9.97	20	PA45	002	25	4	2.9	9.7	600	3.75	0.31	0.63	0.19	0.25	4.38	67.5	13.1	1.88	1.25	0.06	90	1.38	25	0.049	0.312	0.572	0.231	0.068	1400	1340	1380	942	9.45	0.017	81	8
Coal	10.03	20	PA45	003	25	4	1.6	14.9	2510	2.5	0.31	0.63	0.13	4.06	8.13	71.9	14.4	3.13	1.25	0.13	794	1.56	39.4	0.066	0.413	1.14	0.35	0.731	10800	12300	12400	4270	63.20	0.066	82	9
Coal	9.96	20	PA5	001	25	4	4.7	3.1	159	5	0.31	0.63	0.25	0.03	9.38	43.8	5.63	1.88	3.13	0.03	16.8	0.063	0.313	0.197	0.399	0.124	0.256	0.01	372	373	377	263	3.25	0.006	53	10
Coal	9.98	20	PA5	002	25	4	6	18.9	144	3.13	0.31	0.63	0.19	0.03	4.38	42.5	5	4.38	1.88	0.03	22.8	0.125	0.313	0.13	0.423	0.134	0.258	0.008	329	370	375	252	3.66	0.006	54	11
Coal	9.98	20	PA5	003	25	4	2	6.1	3960	2.5	0.31	0.63	0.13	1.69	15.6	334	31.2	6.25	12.5	0.03	1110	1.25	20.6	0.069	1.99	2.91	1.72	0.583	5930	7780	8210	6580	60.70	0.089	55	12
Overburden	9.97	20	BCS3	001	25	4	7.5	14.1	799	4.58	0.31	0.63	0.21	0.08	0.63	254	59	8.75	8.54	0.03	0.313	0.396	0.375	0.125	0.667	0.127	0.013	0.051	1510	1400	1460	1140	14.30	0.026	23	13
Overburden	9.99	20	BCS3	002	25	4	7.1	49.3	754	5	0.31	0.83	0.21	0.15	1.25	281	62.7	7.5	10.4	0.03	0.125	0.771	0.313	0.125	0.777	0.125	0.013	0.033	1700	1500	1550	1130	16.90	0.028	24	14
Overburden	10	20	BCS3	003	25	4	6.7	39.5	1630	30.3	1.78	0.63	0.59	0.38	2.5	527	130	6.25	14.7	0.03	6.53	31.2	1.41	0.125	1.58	0.184	0.084	0.15	2740	2520	2680	2420	27.90	0.050	25	15
Overburden	9.96	20	HCS	001	25	4	3.6	9	4380	3.13	6.97	0.63	0.34	0.21	2.08	379	557	2.5	1.67	0.88	190	44.4	175	0.127	0.746	31.3	2.55	0.477	5770	4180	4600	6310	46.20	0.096	26	16
Overburden	9.99	20	HCS	002	25	4	3.4	14.3	4160	4.38	6.52	0.63	0.65	0.23	1.88	380	543	2.29	1.88	0.81	191	43.1	171	0.133	0.788	29.6	2.49	0.48	5110	4130	4520	6070	45.20	0.094	27	17
Overburden	9.97	20	HCS	003	25	4	1.5	29.8	15200	16.6	27.3	0.63	2.72	111	19.7	447	775	1.88	1.25	1.28	3790	70.9	497	0.125	1.48	57.3	3.88	12	12000	22800	23400	25800	201.00	0.289	28	18
Overburden	10.05	20	KBFWV	001	25	4	7.4	19.9	163	3.13	0.63	0.63	2.13	0.03	1.25	44.4	26.2	2.5	11.9	0.03	0.125	0.031	0.313	0.09	0.554	0.013	0.001	0.004	526	488	489	265	5.53	0.008	29	19
Overburden	10.04	20	KBFWV	002	25	4	7	93.8	150	1.88	0.63	0.63	1.75	0.04	1.88	103	38.1	2.5	13.8	0.03	0.125	0.188	0.313	0.112	1.06	0.018	0.001	0.004	798	809	807	322	11.90	0.013	30	20
Overburden	10.02	20	KBFWV	003	25	4	7.3	74.4	324	3.13	0.31	0.63	0.38	0.03	5.63	153	62.5	2.5	18.1	0.04	0.125	12.5	0.313	0.142	nd	0.015	0.04	0.014	952	1070	1080	594	13.90	0.019	31	21
Overburden	10.01	20	KY1	001	25	4	6.9	5.7	7.85	1.71	0.36	1.14	0.28	0.04	1.42	3.26	1.71	1.71	1.71	0.06	0.152	0.091	0.569	0.033	0.017	0.019	0.003	0.006	141	59	59	24	0.83	0.001	199	22
Overburden	10.01	20	KY1	003	25	4	3.4	4.6	24.2	50.8	29.8	11.9	2.98	0.52	9.92	39.4	15.2	2.98	5.36	0.05	3.83	9.27	23.6	0.76	0.215	0.48	0.367	0.03	464	505	499	294	4.54	0.006	200	23
Overburden	9.99	20	KY2	001	25	4	7.7	5.6	4.18	1.35	0.58	1.16	0.56	0.05	0.79	7.91	4.37	1.16	3.68	0.06	0.29	0.044	0.58	0.035	0.043	0.017	0.002	0.006	106	83	82	30	1.14	0.001	201	24
Overburden	9.99	20	KY2	003	25	4	7	13	20.1	70.4	33.4	12.5	3.14	0.04	2.63	69.9	28.1	1.46	6.27	0.06	0.23	0.617	0.627	0.126	0.229	0.119	0.018	0.005	687	605	590	262	8.03	0.008	202	25
Overburden	10.01	20	KY3	001	25	4	7.2	5.4	88.1	1.67	0.63	1.26	0.9	0.05	0.9	26.1	13.6	1.46	7.74	0.06	0.314	0.036	0.628	0.078	0.2	0.027	0.002	0.006	324	272	271	148	2.74	0.004	203	26
Overburden	10.01	20	KY3	003	25	4	6.5	6.4	746	73.6	17.2	12.8	1.5	0.04	5.45	218	99.5	1.93	15	0.05	0.321	22.2	2.65	0.134	1.06	0.301	0.507	0.054	1670	1550	1600	1240	16.60	0.028	204	27
Overburden	9.99	20	KY4	001	25	4	7	6	121	3.39	0.56	1.2	2.77	0.07	1	31.2	16.4	2.19	10.4	0.06	0.299	0.068	0.598	0.06	0.184	0.031	0.003	0.023	395	347	346	202	3.51	0.005	205	28
Overburden	9.99	20	KY4	003	25	4	4.1	21.7	503	72.4	27.5	12.8	4.21	0.06	16	149	77.5	3.63	21.8	0.08	24.7	29.3	30.3	0.298	0.813	2.53	1.5	0.099	1010	1280	1300	1090	13.40	0.023	206	29
Overburden	10.01	20	KY7	001	25	4	6.2	5.7	1820	2.5	0.31	0.63	0.13	0.03	2.5	358	303	6.88	19.4	0.03	0.188	25.6	0.313	0.066	0.731	0.038	0.029	0.029	2940	2550	2700	2560	27.10	0.053	152	30
Overburden	10.05	20	KY7	002	25	4	6.4	14.6	1830	2.5	0.31	1.25	0.19	0.03	4.38	392	276	7.5	19.4	0.04	0.125	29.8	0.313	0.068	0.838	0.066	0.043	0.028	3130	2580	2740	2590	27.70	0.053	153	31
Overburden	10.02	20	KY7	003	25	4	2.4	16.3	4160	2.5	2.5	1.25	0.13	2.38	30.6	352	511	7.5	4.38	0.19	625	129	62.5	0.038	1.25	4.31	1.01	0.094	6410	5880	6290	6700	57.20	0.103	154	32
Overburden	10.01	20	KY9	001	25	4	6.9	5.3	506	2.5	0.31	0.63	0.13	0.03	1.25	112	53.8	3.13	12.5	0.03	0.188	1.44	0.313	0.103	0.408	0.017	0.005	0.006	1010	929	953	698	8.85	0.016	155	33
Overburden	10	20	KY9	002	25	4	5.8	31.6	613	1.88	0.31	0.63	0.38	0.03	1.25	166	72.5	3.75	15	0.03	2.06	2.94	1.25	0.065	0.444	0.065	0.018	0.004	1180	1150	1180	890	11.40	0.021	156	34
Overburden	10.05	20	KY9	003	25	4	2.7	7.3	1880	3.13	0.31	1.88	0.13	0.38	15	383	178	5	26.9	0.06	132	29.9	20	0.097	0.988	3.44	0.549	0.034	3390	3270	3440	2860	29.40	0.053	157	35
Overburden	9.99	20	LKFC	001	25	4	5	1.8	1390	1.88	0.31	0.63	0.13	0.44	1.25	270	184	9.38	9.58	0.05	2.31	27.3	0.417	0.125	0.537	0.454	0.091	0.067	2270	2000	2120	1920	20.30	0.040	32	36
Overburden	10	20	LKFC	002	25	4	5.1	5.3	999	2.92	0.31	0.63	0.27	0.11	1.25	206	133	6.88	8.54	0.04	1.9	22.1	0.333	0.125	0.423	0.418	0.082	0.041	1760	1580	1650	1400	15.70	0.030	33	37
Overburden	10.01	20	LKFC	003	25	4	2.1	9.8	4660	13.8	8.34	0.63	0.69	3.59	26.6	377	328	3.75	3.75	0.22	778	93.1	76.2	0.125	1.2	8.56	0.7	0.117	5750	7540	8010	7330	65.00	0.105	34	38
Overburden	9.99	20	MKSS	001	25	4	6.8	10	168	1.67	0.31	0.63	1.17	0.11	0.63	51.7	14.2	2.71	10.2	0.03	1.21	0.438	1.46	0.125	0.125	0.271	0.027	0.031	483	430	432	262	4.31	0.007	35	39
Overburden	10	20	MKSS	002	25	4	7.4	56.9	131	1.88	0.31	0.63	1.17	0.11	1.25	96	14.8	3.33	11.9	0.03	0.625	0.479	0.5	0.158	0.194	0.131	0.013	0.031	653	627	627	269	8.66	0.010	36	40
Overburden	10.01	20	MKSS	003	25	4	6.8	65.4	758	26.9	9.81	0.63	1.5	0.19	2.81	347	39.4	2.81	18.1	0.03	5.75	1.06	0.938	0.131	0.583	0.231	0.022	0.04	1640	1650	1710	1230	19.30	0.030	37	41
Overburden	9.96	20	TN2	001	25	4	6.8	16.8	216	5.63	0.31	0.63	2.75	0.03	1.25	63.8	19.4	7.5	17.5	0.03	0.5	0.063	0.313	0.076	0.122	0.014	0.004	0.026	611	570	573	346	6.12	0.009	158	42
Overburden	10.04	20	TN2	002	25	4	7.6	72.5	186	3.75	0.31	1.25	2.19	0.04	4.38	114	27.5	6.25	16.2	0.03	0.125	0.313	0.313	0.084	0.152	0.013	0.004	0.019	815	816	819	371	11.50	0.013	159	43
Overburden	9.99	20	TN2	003	25	4	6.9	56.6	448	4.38	0.38	0.63	0.56	0.05	5	170	48.1	12.5	21.2	0.03	2.06	3.62	0.313	0.099	0.271	0.031	0.033	0.111	1340	1120	1140	724	13.40	0.020	160	44
Refuse	9.98	20	PA12	001	25	4	3.7	3.1	1280	5.63	1.88	0.63	0.56	0.44	13.8	446	35.6	3.13	2.5	0.06	5.25	7.25	13.1	0.102	0.504	0.969	0.289	0.021	2070	1960	2080	1860	18.90	0.037	56	45
Refuse	9.97	20	PA12	002	25	4	3.8	27.3	724	3.13	0.31	0.63	0.44	0.03	5.63	264	11.9	3.13	3.13	0.03	121	1.5	0.313	0.078	0.769	0.274	0.831	0.017	1740	1380	1440	1250	13.10	0.025	57	46
Refuse	10	20	PA12	003	25	4	2.1	8.7	4950	1.88	4.38	0.63	0.31	2.88	79.4	501	75.6	1.25	1.25	0.13	1140	22.1	162	0.036	0.644	2.74	0.623	0.706	6530	7530	8040	8360	64.70	0.107	58	47
Refuse	10.01	20	PA13	001	25	4	2.9	3.1	1640	11.9	0.38	0.63	0.75	0.04	11.9	324	55.6	1.88	1.25	0.38	70.6	11.3	80.6	0.127	0.431	4.31	0.769	0.021	3180	2450	2580	2440	21.20	0.041	59	48
Refuse	10	20	PA13	002	25	4	3	8.8	1580	3.13	0.31	0.63	0.25	0.13	10.6	421	78.8	1.88	1.25	0.13	91.2	6.69	49.4	0.046	0.518	2.59	0.769	0.034	2960	2490	2620	2430	22.80	0.044	60	49
Refuse	9.97	20	PA13	003	25	4	1.8	10	6020	1.25	2.5	0.63	1.38	7.19	25	478	99.4	1.25	1.25	0.19	1690	9.19	118	0.043	0.744	3.9	0.994	0.919	10100	11400	12000	10300	90.20	0.130	61	50
Refuse	9.96	20	PA17	001	25	4	2.6	3.1	2830	3.13	0.31	0.63	5.94	5.44	11.2	234	26.9	2.5	1.25	0.13	788	1.62	65.6	0.153	0.533	0.43	0.185	0.158	3120	3970	4320	4860	36.50	0.066	62	51
Refuse	10	20	PA17	002	25	4	2.7	12	1710	3.75	0.31	0.63	1.06	2.88	3.75	145	18.8	1.88	1.25	0.06	518	1.12	46.2	0.076	0.298	1.38	0.586	0.089	2450	2830	3020	3030	24.10	0.044	63	52
Refuse	10.04	20	PA17	003	25	4	2	3.1	3360	5	2.5	0.63	3.25	5.81	3.13	121	16.9	1.88	1.25	0.04	981	1.06	43.8	0.119	0.289	1.19	0.608	0.44	6430	7120	7480	5560	51.80	0.074	64	53
Refuse	9.98	20	PA22	001	25	4	5.3	3.1	1120	3.75	0.31	0.63	0.19	0.03	5	414	17.5	5	5	0.03	46.4	2	0.313	0.096	1.05	0.256	0.85	0.046	1750	1760	1860	1660	17.30	0.034	65	54
Refuse	9.98	20	PA22	002	25	4	6	8.9	956	3.13	0.63	0.63	0.38	0.03	9.38	388	24.4	1.25	1.25	0.06	2.94	5.5	8.75	0.044	0.434	0.7	0.201	0.013	1300	1580	1660	1430	15.50	0.031	66	55
Refuse	9.99	20	PA22	003	25	4	2.4	3.6	3820	1.88	0.63	0.63	0.38	0.44	19.4	451	95	9.38	3.75	0.06	981	18.9	22.5	0.055	2.75	5.21	4.29	1.14	4660	5520	6000	6420	51.90	0.090	67	56
Refuse	9.96	20	PA30	001	25	4	6.2	4.4	1070	2.5	0.31	0.63	3.75	0.03	5.63	401	15	5	4.38	0.03	42.6	1.81	0.313	0.129	1.09	0.228	0.931	0.04	1640	1720	1810	1610	17.00	0.033	68	57
Refuse	10.05	20	PA30	002	25	4	6.4	26.9	624	3.13	0.31	0.63	0.63	0.03	1.88	202	9.38	2.5	3.13	0.03	128	1.19	0.313	0.106	0.557	0.326	0.825	0.016	1130	1190	1250	1100	12.30	0.022	69	58
Refuse	9.95	20	PA30	003	25	4	3.3	4	1390	3.13	0.31	0.63	3.38	0.06	5	453	52.5	8.75	6.88	0.06	66.2	11.1	3.12	0.047	2.09	2.37	2.35	0.591	2560	2260	2400	2100	21.80	0.041	70	59
Refuse	10.02	20	PA31	001	25	4	6.7	10.3	1300	5	0.31	0.63	1.06	0.03	6.25	410	55.6	76.2	12.5	0.06	0.125	5.56	0.313	0.124	2.84	0.069	0.306	0.064	2180	2080	2200	1880	22.80	0.039	71	60
Refuse	9.96	20	PA31	002	25	4	6.7	24.9	1020	4.38	0.31	0.63	0.44	0.03	6.25	375	45	65.6	10	0.06	0.313	4.88	0.313	0.061	2.39	0.181	0.397	0.054	2010	1830	1920	1540	20.50	0.034	72	61
Refuse	9.99	20	PA31	003	25	4	2.2	9	5100	2.5	1.88	0.63	0.81	2.94	44.4	501	135	86.9	14.4	0.5	1600	31.9	83.8	0.033	4.55	9.31	3.59	0.925	6200	7550	8130	9320	73.90	0.122	73	62
Refuse	9.98	20	PA36	001	25	4	3.3	3.2	1460	5.63	1.25	0.63	0.88	0.03	11.9	238	121	10	1.88	0.5	60.9	20.5	58.1	0.158	1.23	5.73	1.51	0.033	2430	2070	2180	2180	19.60	0.039	74	63
Refuse	9.98	20	PA36	002	25	4	3.4	6.6	1220	3.13	0.38	0.63	0.25	0.03	6.25	262	91.9	5.63	1.25	0.38	43.9	15.2	41.9	0.052	1.27	4.28	1.23	0.027	1930	1850	1940	1830	17.30	0.034	75	64
Refuse	9.98	20	PA36	003	25	4	1.8	8.9	7970	3.13	0.31	0.63	0.31	10	35	398	144	7.5	1.25	0.63	2590	26.6	201	0.04	2.06	9.75	2.11	1.29	11700	12700	13300	14300	110.00	0.167	76	65
Refuse	9.97	20	PA42	001	25	4	6.8	21.4	480	15.6	0.31	0.63	1.06	0.03	5.63	42.5	3.75	188	8.13	0.04	0.25	0.044	0.313	0.198	1.18	0.026	0.008	0.077	1180	1170	1190	751	15.80	0.016	77	66
Refuse	9.96	20	PA42	002	25	4	7	72.5	544	5	0.31	0.63	0.25	0.04	6.88	88.1	8.75	239	11.2	0.03	0.188	0.188	0.313	0.058	1.78	0.013	0.012	0.096	1520	1500	1530	907	22.70	0.022	78	67
Refuse	9.97	20	PA42	003	25	4	2.5	6.9	3040	1.88	0.31	0.63	0.63	0.25	58.1	478	53.8	284	35	0.31	466	7.38	47.5	0.033	6.62	9.94	1.89	1.14	5010	5060	5370	5020	53.10	0.077	79	68
Refuse	10	20	PA48	001	25	4	3.2	3.1	2060	5.63	1.25	0.63	1.13	0.04	11.9	334	144	28.1	3.13	0.63	119	16.2	77.5	0.139	1.71	8.31	1.85	0.031	3150	2690	2870	3090	26.70	0.052	83	69
Refuse	10	20	PA48	002	25	4	3.2	8.9	1950	5	1.25	0.63	0.44	0.06	7.5	352	148	26.9	1.88	0.63	131	16.3	77.5	0.049	1.91	12.4	2.18	0.032	3040	2660	2820	3010	26.40	0.051	84	70
Refuse	9.97	20	PA48	003	25	4	1.7	10.8	8310	6.88	0.63	0.63	1.25	17.8	40.6	436	197	30.6	2.5	0.81	2040	26.1	251	0.038	2.66	13.7	3.36	0.863	12700	14200	14900	13900	116.00	0.164	85	71
Refuse	10.01	20	PA51	001	25	4	3.5	3.3	1130	6.25	0.38	0.63	0.31	0.03	10	349	30	1.88	1.25	0.25	19.6	4.94	31.2	0.112	0.719	2.09	0.266	0.011	1990	1760	1850	1670	16.30	0.032	86	72
Refuse	10.05	20	PA51	002	25	4	4.3	9.6	1030	5	0.31	0.63	0.19	0.03	3.13	348	28.1	1.25	1.25	0.25	16.1	4.62	27.5	0.097	0.713	1.83	0.253	0.008	1610	1580	1650	1530	15.10	0.031	87	73
Refuse	9.97	20	PA51	003	25	4	2.2	9.8	3580	5.63	0.63	0.63	0.13	0.88	23.8	526	56.2	1.25	1.25	0.44	600	10.1	178	0.039	1.32	5.76	0.591	0.331	5930	5910	6230	5910	48.00	0.082	88	74
Refuse	9.97	20	PA58	001	25	4	2.9	3.1	1710	nd	1.25	0.63	4.19	0.13	15	394	81.2	1.88	1.25	0.13	95.6	7.19	50	0.073	0.559	3.01	0.794	0.049	2620	2660	2800	2570	23.80	0.045	89	75
Refuse	9.96	20	PA58	002	25	4	3.1	10.4	1100	nd	nd	0.63	0.88	nd	6.88	244	41.2	nd	1.25	0.31	50.9	8.5	59.4	0.06	0.366	1.69	0.561	0.014	1970	1770	1840	1680	15.10	0.030	90	76
Refuse	10.01	20	PA58	003	25	4	1.9	8.7	4970	nd	0.63	0.63	0.56	6.06	23.1	442	78.1	nd	1.25	0.56	1020	17.4	221	0.043	0.638	7.88	1.23	0.719	7530	9170	9570	8200	69.40	0.105	91	77
Refuse	9.99	20	TNR1	001	25	4	4.8	4.3	943	2.5	0.31	3.13	0.44	0.03	4.38	223	86.2	21.2	41.2	0.06	4.75	3.12	0.313	0.089	0.561	0.913	0.276	0.11	1660	1570	1630	1340	15.80	0.028	161	78
Refuse	9.99	20	TNR1	002	25	4	6.4	9.4	731	2.5	0.31	0.63	0.69	0.03	5	191	59.4	16.9	33.8	0.06	5.5	2.56	0.313	0.062	0.416	0.725	0.214	0.089	1360	1310	1360	1060	13.30	0.023	162	79
Refuse	10.01	20	TNR1	003	25	4	2.5	17	3170	3.75	1.88	0.63	0.88	0.69	58.1	461	206	24.4	59.4	0.38	585	9.81	98.8	0.038	1.28	10.9	1.48	0.498	4770	4840	5140	5440	46.20	0.082	163	80
Refuse	9.98	20	TNR2	001	25	4	7.3	28.9	1410	2.5	0.31	0.63	0.25	0.03	0.63	506	104	3.13	8.75	0.03	1.94	0.938	0.313	0.036	0.531	0.014	0.011	0.087	2390	2230	2360	2050	24.00	0.044	164	81
Refuse	10.03	20	TNR2	002	25	4	7.2	68.8	1300	2.5	0.31	0.63	0.25	0.03	3.75	506	96.9	3.75	7.5	0.03	0.125	1.25	0.313	0.052	0.587	0.026	0.026	0.088	2300	2240	2360	1920	25.80	0.044	165	82
Refuse	10.02	20	TNR2	003	25	4	6.8	29.3	1300	2.5	0.63	2.5	0.13	0.04	3.75	438	127	3.13	11.9	0.04	0.938	1.31	0.313	0.056	0.819	0.05	0.044	0.424	2320	2100	2210	1900	22.60	0.042	166	83
Refuse	10.04	20	TNR3	001	25	4	7.5	23.3	480	6.25	0.44	0.63	3.31	0.04	1.25	89.4	17.5	121	17.5	0.03	0.563	0.313	0.313	0.057	0.138	0.016	0.005	0.054	1300	1130	1150	751	14.40	0.017	167	84
Refuse	10.05	20	TNR3	002	25	4	7.2	43.9	527	6.25	0.44	0.63	2.69	0.03	3.75	116	20	119	17.5	0.03	0.938	0.625	0.313	0.068	0.203	0.023	0.023	0.051	1440	1260	1290	827	16.60	0.019	168	85
Refuse	9.96	20	TNR3	003	25	4	2.4	18.1	3490	4.38	0.31	0.63	0.75	0.75	58.1	414	121	151	41.9	0.31	712	9.81	68.1	0.077	0.644	6.81	0.969	0.525	5570	5480	5850	5890	53.80	0.085	169	86
Refuse	9.97	20	VA16	001	25	4	7.6	3.2	41.2	2.5	0.31	11.9	0.5	0.06	1.25	18.8	3.13	1.25	15	0.03	0.438	0.063	0.313	0.029	0.045	0.02	0.001	0.006	190	180	178	99	1.93	0.002	170	87
Refuse	10	20	VA16	002	25	4	6.8	50.3	35.6	2.5	0.31	0.63	1.94	0.03	3.75	44.4	6.88	1.88	16.9	0.03	0.188	0.625	0.313	0.053	0.118	0.013	0.008	0.003	313	363	360	124	5.51	0.005	171	88
Refuse	10.05	20	VA16	003	25	4	7	62.5	84.4	5	0.44	0.63	0.63	0.05	7.5	78.1	13.1	3.13	21.9	0.03	0.188	1.38	0.313	0.058	0.169	0.077	0.019	0.014	630	563	560	221	8.17	0.009	172	89
Refuse	10	20	VA2	001	25	4	7.2	14.1	486	4.38	0.31	10.6	0.56	0.05	1.25	113	50	6.25	23.8	0.03	0.375	0.375	0.313	0.069	0.869	0.013	0.003	0.048	1020	971	992	701	9.92	0.017	173	90
Refuse	10.04	20	VA2	002	25	4	6.3	41.9	426	4.38	0.31	0.63	1	0.03	4.38	131	52.5	6.25	21.9	0.03	0.375	1.44	0.313	0.079	nd	0.033	0.024	0.035	1070	969	985	656	10.50	0.017	174	91
Refuse	9.96	20	VA2	003	25	4	4.3	7	2160	10	1.88	0.63	2.94	0.06	27.5	468	313	8.75	45.6	0.19	25.1	51.1	33.1	0.081	2.28	6.09	1.22	0.182	3560	2970	3160	3280	32.40	0.063	175	92
Refuse	10	20	VA3	001	25	4	5.9	4.6	63.8	5	0.31	8.13	0.5	0.04	3.75	7.5	8.13	3.75	10.6	0.03	0.375	1.62	0.313	0.082	0.063	0.067	0.027	0.003	212	195	194	117	1.96	0.003	176	93
Refuse	9.99	20	VA3	002	25	4	6.4	7.5	65.6	3.13	0.31	0.63	1.19	0.03	3.75	10	8.75	3.75	8.75	0.03	0.125	1.69	0.313	0.068	0.106	0.067	0.029	0.003	187	203	203	114	2.15	0.003	177	94
Refuse	9.98	20	VA3	003	25	4	2.4	152	251	7.5	0.31	0.63	1.69	2.06	16.2	65.6	45	4.38	37.5	0.06	103	22.3	125	0.569	0.432	1.2	0.688	0.039	998	2700	2640	1030	15.70	0.031	178	95
Refuse	10	20	VA6	001	25	4	7.4	6.3	43.1	1.88	0.31	1.88	0.63	0.03	1.25	13.8	3.75	1.25	1.25	0.03	0.25	0.031	0.313	0.033	0.038	0.013	0.001	0.004	516	147	147	73	1.60	0.002	179	96
Refuse	10	20	VA6	002	25	4	7.2	56.1	186	4.38	0.31	0.63	1.81	0.04	4.38	91.2	26.9	5	8.13	0.03	0.25	0.5	0.313	0.06	0.196	0.015	0.004	0.011	609	698	700	337	9.22	0.011	180	97
Refuse	9.97	20	VA6	003	25	4	6.9	23.8	504	3.75	0.44	0.63	1.69	0.03	5.63	151	52.5	5.63	9.38	0.03	0.375	11.3	0.313	0.083	0.351	0.034	0.049	0.111	1330	1040	1070	761	11.00	0.019	181	98

Refuse	9.95	20	WV5	001	25	4	7.8	17.6	16.9	2.5	0.31	0.63	2.19	0.05	0.31	10.6	3.75	1.25	10.6	0.03	0.25	0.044	0.313	0.113	0.074	0.032	0.002	0.004	145	168	167	58	2.56	0.002	182	99
Refuse	9.96	20	WV5	002	25	4	6.7	55.6	18.8	1.88	0.31	0.63	2.13	0.03	1.88	30.6	10	2.5	13.1	0.03	4.5	0.563	0.313	0.216	0.135	0.023	0.016	0.003	273	327	323	100	5.27	0.005	183	100
Refuse	9.97	20	WV5	003	25	4	7.3	110	73.1	5.63	0.44	0.63	2.44	0.03	7.5	109	36.9	3.13	20.6	0.03	0.813	0.563	0.438	0.232	0.364	0.051	0.044	0.024	620	841	835	271	13.50	0.013	184	101
RefuseU	9.98	20	TGS1	001	25	4	6.3	3.6	651	36.9	2.5	3.13	2.88	0.03	5	5	1.88	356	10	0.04	0.375	0.063	0.313	0.055	0.906	0.039	0.015	0.05	1520	1660	1690	1090	23.90	0.022	92	102
RefuseU	9.96	20	TGS1	002	25	4	5	10.9	696	34.4	0.5	0.63	1.38	0.04	5.63	4.38	1.88	348	9.38	0.06	46.7	0.125	3.12	0.062	0.894	0.057	0.022	0.032	1760	1680	1720	1210	23.90	0.023	93	103
RefuseU	10.02	20	TGS1	003	25	4	2.1	12.9	5320	25.6	10.6	0.63	0.63	29.9	112	335	83.8	731	86.2	1.25	1200	13	153	0.08	10.6	21.2	4.24	0.825	9150	9250	9680	9550	102.00	0.128	94	104
RefuseU	10.05	20	TGS10A	001	25	4	2.2	3.1	69200	25.6	3.13	6.25	1.25	3.5	0.63	296	230	137	26.2	1.56	32300	10.5	1300	0.125	6.01	49.4	42.8	0.031	31100	38200	39900	151000	677.00	1.320	125	105
RefuseU	9.98	20	TGS10A	002	25	4	2.3	4.6	64900	6.88	0.31	0.63	0.31	2.13	3.13	16.9	244	131	49.4	1.13	31000	15.9	1300	0.041	4.64	45.7	38.9	0.018	32100	35800	37700	142000	632.00	1.240	126	106
RefuseU	9.98	20	TGS10A	003	25	4	2.1	4.1	67700	16.2	0.63	0.63	0.63	5.63	2.5	391	224	107	1.25	1.5	29600	10.7	1280	0.125	4.68	54.9	42.9	0.198	31900	37300	39600	143000	646.00	1.250	127	107
RefuseU	9.96	20	TGS10B	001	25	4	2.9	3.4	7160	3.13	2.5	1.25	0.38	2.63	4.38	218	208	694	4.38	1.25	1940	5.12	451	0.026	8.56	29.8	9.12	0.038	9350	7250	7850	13500	98.80	0.159	128	108
RefuseU	9.97	20	TGS10B	002	25	4	2.9	7.2	5210	4.38	3.13	0.63	0.19	1.44	3.75	162	171	625	5.63	1.13	1120	4	324	0.03	6.5	21.4	7.31	0.03	7060	5910	6330	9360	77.60	0.118	129	109
RefuseU	9.99	20	TGS10B	003	25	4	1.9	8.3	8830	9.38	1.88	0.63	0.19	51.2	25	352	246	681	1.25	1.56	2080	5.75	568	0.032	10.6	nd	10.2	0.8	11000	12500	13000	16000	131.00	0.186	130	110
RefuseU	9.99	20	TGS11	001	25	4	7.1	6.5	319	16.2	0.31	0.63	0.13	0.03	3.13	1.88	0.31	161	3.13	0.03	0.813	0.013	0.313	0.038	0.088	0.024	0.004	0.731	906	825	837	509	11.30	0.011	131	111
RefuseU	10	20	TGS11	002	25	4	6.7	22.3	341	12.5	0.31	0.63	0.5	0.03	6.25	1.25	0.56	209	3.75	0.06	2.62	0.019	0.625	0.033	0.152	0.067	0.019	0.869	1040	974	988	585	14.50	0.013	132	112
RefuseU	9.97	20	TGS11	003	25	4	2.9	114	624	16.9	0.56	0.63	1.31	0.25	41.9	8.13	3.13	399	25	0.38	100	0.038	15.6	0.314	1.78	0.398	0.129	1.9	2000	2150	2180	1360	27.20	0.024	133	113
RefuseU	9.98	20	TGS12	001	25	4	2.5	4.3	3940	8.13	20	0.63	2	3.56	3.13	292	186	83.8	1.25	0.63	781	10.5	211	0.048	6.09	4.06	2.14	0.008	7220	5070	5450	6700	50.00	0.091	134	114
RefuseU	10	20	TGS12	002	25	4	2.5	7.6	5210	11.2	25	0.63	0.25	5.69	3.13	430	281	138	1.88	0.94	1200	15.6	318	0.037	8.44	4.76	3.51	0.014	6890	6160	6640	9420	66.60	0.123	135	115
RefuseU	10.04	20	TGS12	003	25	4	1.3	9.9	20400	27.5	94.4	0.63	3.13	1120	61.2	438	229	124	3.75	0.81	8190	21.4	392	0.044	13.6	9.12	4.31	0.725	29300	33100	33600	39500	295.00	0.396	136	116
RefuseU	10.05	20	TGS13	001	25	4	7.5	25.3	46.9	28.1	0.31	0.63	0.44	0.03	1.25	43.8	4.38	14.4	7.5	0.03	2.06	0.013	0.5	0.068	0.564	0.021	0.007	0.004	340	373	370	155	5.26	0.005	137	117
RefuseU	9.96	20	TGS13	002	25	4	6.9	161	41.2	19.4	0.31	0.63	0.38	0.03	3.13	209	8.75	15.6	8.75	0.03	3.31	0.125	0.313	0.074	1.31	0.031	0.008	0.004	974	1040	1040	316	17.30	0.017	138	118
RefuseU	10.05	20	TGS13	003	25	4	6.9	141	523	30.6	2.5	0.63	1.13	3.75	15.6	462	18.1	22.5	15.6	0.03	28.1	0.188	8.12	0.101	2.68	0.069	0.04	0.043	1350	1840	1880	1170	25.10	0.034	139	119
RefuseU	10.04	20	TGS14	001	25	4	2.9	3.2	7690	10	2.5	1.88	0.56	1.94	3.13	306	154	281	3.13	1.44	2710	7.19	464	0.029	10.5	10.3	9	0.024	9170	7060	7830	15200	90.80	0.170	140	120
RefuseU	10.05	20	TGS14	002	25	4	3.1	3.6	7880	11.2	3.13	0.63	0.19	1.5	3.13	286	150	275	3.75	1.44	2310	6.81	445	0.039	10	10.8	8.38	0.022	6990	6740	7590	14500	86.30	0.162	141	121
RefuseU	9.95	20	TGS14	003	25	4	1.6	5.5	21400	26.9	31.9	9.38	3.56	1030	49.4	556	167	316	12.5	1.63	8500	15.9	591	0.049	21.2	24.6	12.2	0.931	20900	23600	24900	41900	261.00	0.405	142	122
RefuseU	10.01	20	TGS15	001	25	4	3.8	3.3	1970	21.9	0.63	6.25	0.13	0.03	5.63	116	52.5	731	24.4	0.56	93.1	1.06	14.4	0.036	8.38	2.53	1.54	0.03	4190	3770	3890	3160	54.00	0.058	143	123
RefuseU	10.04	20	TGS15	002	25	4	3.8	3.1	1990	18.8	0.44	0.63	0.63	0.03	5.63	104	48.8	611	23.8	0.5	91.2	1.06	13.8	0.071	7.12	2.45	1.28	0.031	3140	3550	3680	3030	48.70	0.055	144	124
RefuseU	9.98	20	TGS15	003	25	4	1.8	9	5230	29.4	3.75	0.63	0.25	2.38	40.6	209	106	756	22.5	0.75	781	3.81	114	0.031	11.8	9.69	3.29	0.228	11000	12000	12300	8290	109.00	0.116	145	125
RefuseU	9.96	20	TGS16	001	25	4	2.9	4.8	3820	36.2	31.2	3.13	0.63	1.19	6.88	491	98.1	414	13.8	0.5	688	3.88	142	0.044	11	3.82	2.18	0.017	6150	5160	5560	6700	63.60	0.099	146	126
RefuseU	10.03	20	TGS16	002	25	4	2.9	4.3	3940	38.8	31.9	0.63	0.75	3.56	6.25	498	99.4	420	13.8	0.56	781	3.75	132	0.048	13.2	3.86	2.17	0.018	5480	5290	5720	6980	65.70	0.102	147	127
RefuseU	9.97	20	TGS16	003	25	4	1.4	6.2	17100	75.6	0.31	0.63	1.19	1360	106	434	134	473	38.8	0.63	7000	11.3	401	0.183	6.94	16.2	4.04	0.499	22400	27800	28400	33800	258.00	0.341	148	128
RefuseU	9.95	20	TGS17	001	25	4	7.2	24.3	356	28.1	3.75	3.75	0.38	0.06	4.38	3.75	0.63	254	9.38	0.03	44	0.019	3.75	0.025	0.189	0.083	0.066	0.016	1420	1160	1170	761	18.00	0.015	149	129
RefuseU	9.99	20	TGS17	002	25	4	8.4	182	214	46.9	4.38	0.63	0.81	0.03	3.75	46.2	3.13	380	16.9	0.03	0.625	0.063	0.313	0.037	1.21	0.014	0.004	0.013	1880	1830	1840	722	36.30	0.023	150	130
RefuseU	10.01	20	TGS17	003	25	4	6.7	46	1230	28.8	3.13	0.63	0.25	0.63	3.75	264	15.6	411	31.9	0.04	11.6	0.375	0.625	0.101	4.61	0.128	0.077	0.03	4440	2660	2750	2020	37.70	0.042	151	131
RefuseU	7.48	14.97	TGS2A	001	25	4	2.5	4.2	36100	2.51	0.67	1.67	6.85	2.09	4.18	76.8	34.2	63.5	29.2	1.84	18200	4.51	1030	0.045	2.25	2.02	1.79	0.036	23700	22100	24600	78500	353.00	0.703	95	132
RefuseU	7.5	15	TGS2A	002	25	4	2.4	5.3	42500	4.17	0.83	0.83	0.67	2.42	4.17	883	38.3	80	53.3	2.5	21800	6	1300	0.057	2.49	2.54	2.5	0.047	27200	26000	27900	95300	429.00	0.855	96	133
RefuseU	7.46	14.92	TGS2A	003	25	4	2.2	6	57600	14.2	0.59	0.84	0.67	4.27	5.86	135	51.1	77.9	16.8	2.6	27900	7.12	1490	0.034	3.48	3.49	2.86	0.48	26400	32700	34500	127000	556.00	1.090	97	134
RefuseU	9.98	20	TGS2B	001	25	4	3.4	3.1	1890	6.25	0.63	1.88	0.19	0.03	3.75	75	78.1	493	28.8	0.56	87.5	1.62	58.1	0.043	9.56	4.99	5.41	0.073	3370	3180	3300	2930	41.70	0.050	98	135
RefuseU	10	20	TGS2B	002	25	4	3.4	5.8	1730	6.88	0.63	0.63	0.63	0.06	3.13	68.1	73.8	458	26.9	0.56	62.2	1.62	56.9	0.066	6.81	3.23	2.51	0.083	3300	2960	3060	2670	38.60	0.046	99	136
RefuseU	9.98	20	TGS2B	003	25	4	1.9	11.8	3980	13.1	1.88	0.63	0.13	0.31	23.1	76.2	83.8	407	26.9	0.56	675	2.75	121	0.039	9.25	8.75	3.22	0.41	10200	9100	9370	6290	75.50	0.087	100	137
RefuseU	10.05	20	TGS3	001	25	4	7	53.9	234	101	10	3.75	0.81	0.05	2.5	5.63	0.56	292	13.8	0.03	2.62	0.013	0.625	0.034	0.286	0.015	0.004	0.01	1380	1310	1320	675	22.70	0.015	101	138
RefuseU	10.03	20	TGS3	002	25	4	8	186	197	97.5	8.75	0.63	0.75	0.03	3.75	65.6	3.13	364	22.5	0.03	1.81	0.063	0.313	0.049	1.48	0.013	0.007	0.004	1870	1930	1940	771	37.80	0.024	102	139
RefuseU	9.95	20	TGS3	003	25	4	7.5	70	2010	51.9	1.25	0.63	0.38	0.03	8.13	562	23.8	466	55.6	0.06	1.06	0.938	0.313	0.178	10.1	0.209	0.149	0.033	4600	3790	3980	3190	53.50	0.064	103	140
RefuseU	10	20	TGS4	001	25	4	8.3	3.8	1.31	1.88	0.31	0.63	0.75	0.03	0.31	0.31	0.31	0.63	1.25	0.03	0.188	0.013	0.313	0.022	0.013	0.013	0.001	0.003	581	32	32	12	0.54	0.000	104	141
RefuseU	9.98	20	TGS4	002	25	4	7.3	81.9	56.2	16.2	0.31	0.63	0.19	0.03	5	1.88	0.63	144	6.25	0.03	0.125	0.056	0.313	0.027	0.15	0.013	0.002	0.003	683	679	683	233	13.70	0.008	105	142
RefuseU	9.97	20	TGS4	003	25	4	3.1	10.3	2380	11.2	1.25	1.88	0.25	0.13	84.4	255	117	455	78.8	0.56	114	54.4	70.6	0.153	14.3	12.9	2.05	0.063	3800	3880	4050	3910	49.00	0.064	106	143
RefuseU	10.04	20	TGS5	001	25	4	2.6	nd	2250	2.5	0.31	1.25	0.69	7	0.56	99.4	1.25	6.88	2.5	0.03	1060	1.12	22.5	0.173	1.21	0.411	0.744	0.006	3270	3650	3960	4480	33.50	0.060	107	144
RefuseU	9.95	20	TGS5	002	25	4	2.6	8	2310	2.5	0.31	0.63	1.13	7.06	0.63	30	1.88	9.38	3.13	0.04	1110	1.06	27.5	0.223	1.2	0.396	0.825	0.007	3140	3650	3960	4590	33.50	0.060	108	145
RefuseU	9.96	20	TGS5	003	25	4	1.7	7.6	11800	8.13	2.5	0.63	0.31	46.3	2.5	175	5.63	21.9	6.88	0.06	4640	4.62	70.6	0.091	5.2	1.61	2.23	0.285	10700	16500	17600	21500	157.00	0.228	109	146
RefuseU	10	20	TGS6	001	25	4	6	4.4	688	28.8	0.63	1.25	0.56	0.03	3.13	3.13	1.25	380	8.75	0.19	0.188	0.05	0.313	0.072	0.596	0.046	0.012	0.146	1770	1710	1740	1120	24.70	0.023	110	147
RefuseU	10.02	20	TGS6	002	25	4	7.1	7	613	28.1	0.56	0.63	0.25	0.03	5	3.13	1.25	311	7.5	0.13	0.188	0.125	0.313	0.06	0.333	0.031	0.009	0.109	1650	1500	1530	974	21.30	0.020	111	148
RefuseU	9.99	20	TGS6	003	25	4	3	12.7	1570	23.8	1.88	0.63	0.56	0.31	31.9	36.9	13.8	650	39.4	0.69	156	0.5	6.88	0.069	5.68	1.42	0.208	0.406	3980	3560	3650	2700	48.00	0.048	112	149
RefuseU	9.98	20	TGS7A	001	25	4	7.6	18.3	969	55	1.88	1.25	0.31	0.03	1.88	111	8.13	392	21.2	0.04	0.125	0.031	0.313	0.045	3.86	0.016	0.003	0.009	2390	2240	2290	1570	31.70	0.032	113	150
RefuseU	10.01	20	TGS7A	002	25	4	7.4	131	924	51.2	1.25	0.63	0.38	0.04	5	228	14.4	369	23.1	0.03	0.125	0.188	0.313	0.063	4.94	0.057	0.021	0.008	2600	2550	2620	1620	40.30	0.039	114	151
RefuseU	9.98	20	TGS7A	003	25	4	7.3	82.5	1890	55	0.31	0.63	0.38	0.13	3.75	459	38.1	457	38.8	0.06	0.25	0.938	0.313	0.113	nd	0.572	0.32	0.126	3720	3620	3790	2960	51.60	0.061	115	152
RefuseU	9.96	20	TGS7B	001	25	4	3.9	4.2	1150	3.75	1.25	1.25	0.25	0.44	0.31	188	24.4	48.1	3.75	0.06	231	1.62	20.6	0.079	2.89	1.12	0.408	0.004	1900	1750	1860	1930	18.00	0.033	116	153
RefuseU	9.98	20	TGS7B	002	25	4	4.2	9.5	752	7.5	0.63	0.63	0.31	0.13	1.88	119	16.9	28.1	2.5	0.06	151	1.06	15.6	0.051	1.73	0.631	0.241	0.003	1180	1240	1300	1270	12.20	0.023	117	154
RefuseU	9.97	20	TGS7B	003	25	4	1.5	14.9	19700	11.2	25	0.63	0.31	342	17.5	555	53.8	101	15	0.19	6380	6.94	107	0.08	9.81	7.19	1.69	0.226	26800	25200	26500	33900	252.00	0.343	118	155
RefuseU	9.95	20	TGS8	001	25	4	3.1	4.8	7650	3.13	0.31	1.25	2.63	0.63	0.31	249	25.6	79.4	15	0.25	3860	5.12	108	0.062	4.48	5.13	6.69	0.016	8320	7210	8310	15900	93.00	0.179	119	156
RefuseU	9.98	20	TGS8	002	25	4	3.1	7.3	6580	3.13	0.31	0.63	0.38	0.5	3.13	161	25	68.8	8.13	0.19	3190	4.44	98.1	0.062	3.51	nd	5.35	0.009	7150	6360	7320	13400	79.20	0.153	120	157
RefuseU	9.96	20	TGS8	003	25	4	2	6.5	11600	6.25	0.56	0.63	0.31	5.69	2.5	321	37.5	96.2	1.25	0.38	4410	7.69	149	0.026	4.76	7.94	8.62	0.191	8120	12700	14000	21400	140.00	0.230	121	158
RefuseU	10.05	20	TGS9	001	25	4	5.2	3.8	684	4.38	0.31	0.63	0.31	0.03	1.88	6.25	4.38	339	9.38	0.25	3.25	0.05	0.313	0.071	1.54	0.112	0.165	0.293	1610	1590	1620	1060	22.20	0.022	122	159
RefuseU	10.02	20	TGS9	002	25	4	5.6	8.5	630	3.75	0.31	0.63	0.13	0.03	3.75	6.88	5	289	8.75	0.19	0.5	0.05	0.313	0.054	1.12	0.083	0.133	0.241	1490	1430	1460	952	19.60	0.020	123	160
RefuseU	10.01	20	TGS9	003	25	4	2.2	14.9	2810	3.75	1.88	0.63	0.25	0.56	35.6	88.8	50.6	522	39.4	0.75	448	0.75	48.8	0.053	6.75	2.42	2.11	3.8	6830	6240	6440	4570	61.70	0.070	124	161
Pyrite	10.01	20	SKYPA	001	25	4	2.8	3.9	4420	5.63	0.38	0.63	0.13	1.63	0.31	56.2	27.5	0.63	1.88	0.25	862	0.438	535	0.034	0.104	17.9	0.994	0.003	4640	3750	4060	7770	35.90	0.082	38	162
Pyrite	10.05	20	SKYPA	002	25	4	2.8	20.4	3490	5	0.31	0.63	0.13	1.06	1.25	1.88	23.8	0.63	1.88	0.19	762	0.313	428	0.074	0.188	15.9	0.906	0.003	4330	3270	3510	6260	30.10	0.068	39	163
Pyrite	9.96	20	SKYPA	003	25	4	1.5	8.1	20400	9.38	0.31	3.13	0.13	9.13	9.38	248	36.2	6.25	12.5	0.44	5860	0.75	781	0.071	0.181	20.7	2.69	0.018	21200	24200	25200	35200	231.00	0.331	40	164
Shale	9.97	20	Morris1	001	25	4	7.4	23.7	33.8	150	0.38	0.63	0.25	0.06	3.13	56.9	1.88	53.8	21.2	0.04	0.375	0.013	0.313	0.42	11.4	0.014	0.001	0.003	655	734	726	325	10.80	0.008	41	165
Shale	10.05	20	Morris1	002	25	4	6.8	129	15	49.4	0.31	0.63	0.13	0.06	1.25	150	3.13	25.6	11.2	0.03	0.125	0.063	0.313	0.598	8.69	0.019	0.001	0.003	801	881	873	259	14.60	0.013	42	166
Shale	9.98	20	Morris1	003	25	4	6.9	137	1280	127	8.75	1.25	0.44	0.04	10	838	26.2	67.5	41.9	0.06	2.81	0.25	1.88	0.222	13.9	0.086	0.03	0.053	2460	3110	3260	2420	41.30	0.058	43	167
Shale	10.01	20	Morris2	001	25	4	7.9	18	16.9	99.4	0.31	0.63	0.81	0.04	1.88	43.1	1.25	29.4	8.75	0.03	0.313	0.013	0.313	0.49	6.62	0.013	0.001	0.003	392	492	486	207	7.15	0.006	44	168
Shale	10.01	20	Morris2	002	25	4	6.8	143	28.1	167	0.31	0.63	0.19	0.13	2.5	188	5	53.1	20.6	0.03	0.125	0.063	0.313	0.622	14.7	0.013	0.001	0.003	1150	1320	1310	468	21.30	0.018	45	169
Shale	9.95	20	Morris2	003	25	4	6.9	141	1610	209	0.56	2.5	0.31	0.04	8.75	1000	36.2	97.5	56.2	0.13	0.875	0.375	0.625	0.087	17.2	0.093	0.033	0.081	2700	3740	3930	3040	50.20	0.070	46	170
Shale	9.95	20	Morris3	001	25	4	7.5	18.9	18.8	92.5	0.31	0.63	0.13	0.06	2.5	40.6	0.63	29.4	10	0.03	0.125	0.013	0.313	0.473	6.44	0.013	0.001	0.003	397	472	466	197	6.90	0.005	47	171
Shale	10.04	20	Morris3	002	25	4	7	164	54.4	304	0.38	0.63	0.13	0.13	5	241	7.5	96.2	38.8	0.06	0.125	0.056	0.313	0.581	21.2	0.024	0.001	0.003	1750	1910	1900	750	31.20	0.025	48	172
Shale	10.04	20	Morris3	003	25	4	6.7	90	1730	185	0.63	1.25	0.25	0.04	6.25	881	35.6	105	56.2	0.13	10.5	0.313	1.88	0.069	15.8	0.082	0.024	0.073	3140	3500	3700	3040	44.80	0.065	49	173
Shale	7.44	14.88	EGSP01	001	25	4	6.6	4.2	849	134	0.42	0.84	0.17	0.04	4.2	284	24.4	171	69.7	0.17	4.37	0.067	0.42	0.066	7.48	0.051	0.002	0.018	2180	2080	2140	1550	26.20	0.032	185	174
Shale	7.44	14.88	EGSP01	003	25	4	7.5	76.8	1620	160	4.2	8.4	1.68	0.04	7.56	671	55.4	220	122	0.42	0.252	0.168	1.68	0.174	4.29	0.038	0.013	0.094	3930	3540	3700	2890	47.90	0.061	186	175
Shale	10.01	20	JKLM01	001	25	4	7.5	13.6	50.6	419	0.56	3.13	0.13	0.04	3.13	151	7.5	180	101	0.06	0.125	0.025	0.438	0.442	7.75	0.026	0.001	0.003	1810	1840	1830	918	27.80	0.021	187	176
Shale	10.02	20	JKLM01	003	25	4	7.2	63.1	1840	706	3.13	6.25	1.25	0.06	6.25	1120	56.2	323	188	0.25	0.188	0.75	0.625	0.082	14.7	0.183	0.083	0.149	6750	5480	5680	4280	77.90	0.091	188	177
Shale	6.87	13.74	JKLM02	001	25	4	7.4	14.3	62.8	573	0.64	4.55	0.18	0.07	4.55	232	10	238	118	0.09	0.182	0.036	0.455	0.324	9.37	0.038	0.002	0.006	2810	2460	2450	1250	37.40	0.029	189	178
Shale	6.84	13.68	JKLM02	003	25	4	7.3	50.3	1930	868	4.57	9.14	1.83	0.05	6.4	1200	60.3	366	205	0.27	0.183	0.731	0.457	0.154	15.1	0.118	0.071	0.126	7390	6010	6220	4680	86.30	0.098	190	179
Shale	10.01	20	JKLM03	001	25	4	7.6	3.1	60	400	0.31	3.13	0.13	0.04	3.13	156	9.38	202	119	0.13	0.125	0.025	0.313	0.345	7.81	0.027	0.001	0.003	2230	1870	1860	956	28.20	0.021	191	180
Shale	10.04	20	JKLM03	003	25	4	7.4	43.3	1830	638	3.13	6.25	1.25	0.03	5.63	1040	59.4	302	186	0.25	0.125	0.688	0.313	0.046	14.1	0.156	0.094	0.146	6930	5170	5370	4100	72.30	0.086	192	181
Shale	10	20	JKLM04	001	25	4	7.7	10.8	204	412	0.56	3.13	0.13	0.04	3.13	153	8.75	179	105	0.13	0.125	0.025	0.375	0.251	7.25	0.068	0.001	0.003	2030	1970	1960	1070	28.60	0.023	193	182
Shale	10	20	JKLM04	003	25	4	7.5	46.4	829	700	3.13	6.25	1.25	0.03	3.13	504	29.4	153	94.4	0.13	0.125	0.375	0.313	0.015	6.56	0.099	0.044	0.071	7310	3590	3640	2340	49.60	0.050	194	183
Shale	7.9	15.8	JKLM05	001	25	4	7.1	13.6	97.3	451	0.4	3.16	0.16	0.04	3.96	174	11.1	214	123	0.08	0.158	0.024	0.396	0.17	12.2	0.016	0.002	0.004	2180	2100	2090	1080	31.70	0.024	195	184
Shale	7.9	15.8	JKLM05	003	25	4	7.3	46.2	2020	736	3.96	7.91	1.58	0.04	6.33	1120	63.3	322	206	0.32	0.158	0.712	0.396	0.085	16.9	0.153	0.093	0.168	6900	5630	5850	4520	79.30	0.093	196	185
Shale	7.01	14.02	OH01	001	25	4	6.5	12.4	1130	624	0.45	4.46	0.18	0.04	4.46	410	59.7	483	123	0.09	0.178	0.267	0.446	0.099	3.11	0.018	0.002	0.011	5320	4110	4190	2850	60.60	0.057	197	186
Shale	7.01	14.02	OH01	003	25	4	7.9	44	1540	651	4.46	8.92	1.78	0.04	4.46	605	115	563	157	0.27	0.178	1.78	0.446	0.086	4.16	0.051	0.041	0.065	6440	5040	5160	3680	75.90	0.076	198	187

Table SI-5. Sample descriptions and associated PHREEQC input and output data for blank samples: type 1 (deionized water), type 2 (10% CO2), and type 3 (30% H2O2+10% CO2).

[element concentrations corrected for dilution of initial leach volume to 100 ml; concentration values originally reported as less than detection limit shown equal to the detection limit; nd, no data]

SORT

1 1

ROCKTYPE	MASS	VOL	SAMPLE	LEACH	TEMPC	pe	pH	TIC	SO4	Cl	F	Br	NO3N	P	Si	Ca	Mg	Na	K	Li	Fe	Mn	Al	Ba	Sr	Zn	Co	Se	Sp. Conduct., µS/cm at 25 °C			TDS	OSMP	IonStr	2
Class	g	ml	Name	Type	C			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	Measured	McCleskey	PHREEQC	mg/L	mOsm/kg	mol/L	3
n.a.	0	20	Blank	001	25	4	6	1.4	3.38	2.29	0.31	0.63	0.13	0.05	0.38	1.15	0.4	3.96	1.46	0.03	0.271	0.027	0.313	0.644	0.125	0.144	0.013	0.031	16.5	31.6	31.5	16.0	0.43	0.0000	4
n.a.	0	20	Blank1	001	25	4	4.8	3.8	3.75	3.75	0.31	0.63	1.19	0.03	11.9	1.25	0.31	1.25	1.25	0.03	0.25	0.013	0.313	0.143	0.045	0.013	0.008	0.003	13.0	37.5	37.3	31.1	0.41	0.0000	7
n.a.	0	20	Blank2	001	25	4	5.7	4	11.2	1.88	0.31	1.25	0.63	0.03	1.25	2.5	0.31	1.25	1.25	0.03	0.5	0.019	0.313	0.043	0.038	0.036	0.003	0.003	26.0	44.0	43.9	26.0	0.47	0.0010	10
n.a.	0	20	Blank3	001	25	4	6.8	3.9	15	1.88	0.31	0.63	0.13	0.25	0.31	1.25	0.31	0.63	1.25	0.03	4.06	0.063	0.438	0.027	0.013	0.027	0.012	0.003	8.0	54.7	55.3	31.3	0.65	0.0010	13
n.a.	0	20	Blank4	001	25	4	7	45.4	73.1	19.4	1.88	0.63	0.19	0.06	1.25	0.31	0.31	119	3.75	0.03	0.438	0.013	0.625	0.026	0.034	0.013	0.001	0.003	5.0	532.0	535.0	223.0	9.82	0.0060	16
n.a.	0	20	Blank5	001	25	4	4.1	8.3	3.75	6.25	3.75	0.63	0.13	0.06	3.13	0.63	0.31	1.25	1.25	0.03	0.125	0.013	0.313	0.031	0.034	0.019	0.001	0.003	85.0	65.7	65.5	22.7	0.59	0.0000	19
n.a.	0	20	Blank6	001	25	4	7	5.8	1.74	5.81	0.58	1.16	0.29	0.06	0.41	0.41	0.58	0.58	2.91	0.06	0.291	0.023	0.581	0.031	0.029	0.026	0.003	0.006	8.0	144.0	144.0	17.8	1.68	0.0020	21
			Median				6.0																						13	55	55	26			
			Min				4.1																						5	32	32	16			
			Max				7.0																						85	532	535	223			
n.a.	0	20	Blank	002	25	4	5.1	5.8	14.8	1.88	0.31	0.63	0.13	0.1	0.31	2.15	2	4.17	3.13	0.03	0.646	0.196	0.708	0.525	0.125	0.191	0.017	0.031	52.7	63.5	63.4	33.5	0.68	0.0010	5
n.a.	0	20	Blank1	002	25	4	4.4	14.7	11.2	2.5	0.31	0.63	0.13	0.03	3.75	1.25	0.31	1.25	1.25	0.03	1.44	0.013	1.25	0.042	0.06	0.052	0.007	0.003	45.0	54.5	54.5	29.5	0.44	0.0010	8
n.a.	0	20	Blank2	002	25	4	4.8	6.1	3.75	1.88	0.31	0.63	0.31	0.03	0.63	1.25	0.31	0.63	1.25	0.03	0.375	0.013	0.313	0.026	0.019	0.014	0.003	0.003	15.0	28.1	28.0	13.7	0.27	0.0000	11
n.a.	0	20	Blank3	002	25	4	5.8	15.4	5.63	3.13	0.31	0.63	0.13	0.03	1.88	1.25	0.31	5	1.25	0.03	0.125	0.013	0.313	0.04	0.048	0.013	0.003	0.003	25.0	48.4	48.3	21.2	0.76	0.0010	14
n.a.	0	20	Blank4	002	25	4	6.3	35.2	0.94	1.25	0.31	0.63	0.19	0.03	0.31	1.25	0.31	22.5	1.25	0.03	0.125	0.013	0.313	0.032	0.023	0.035	0.001	0.003	90.0	122.0	122.0	30.8	2.54	0.0010	17
			Median				5.1																						45	55	55	30			
			Min				4.4																						15	28	28	14			
			Max				6.3																						90	122	122	34			
n.a.	0	20	Blank	003	25	4	2	6.1	49.5	3.75	37.5	0.63	2.66	0.42	0.38	12.1	3.66	0.63	1.56	0.03	3.97	0.809	0.906	0.125	0.125	0.15	0.013	0.031	422.0	3850.0	3850.0	133.0	12.40	0.0070	6
n.a.	0	20	Blank1	003	25	4	3.6	4.3	15	1.25	221	1.25	20.3	0.31	0.63	1.25	0.31	1.25	1.25	0.03	2.56	0.031	0.5	0.021	0.024	0.049	0.006	0.003	46.0	674.0	663.0	339.0	10.50	0.0060	9
n.a.	0	20	Blank2	003	25	4	2.6	10	26.2	1.25	216	0.63	0.13	3.25	3.13	2.5	0.31	1.88	5	0.03	7.5	0.025	0.625	0.056	0.071	0.079	0.012	0.003	227.0	1120.0	1120.0	274.0	5.80	0.0040	12
n.a.	0	20	Blank3	003	25	4	2.7	12.5	3.75	1.25	213	0.63	3.13	0.03	0.31	0.63	0.31	1.25	1.25	0.03	0.25	0.013	0.313	0.035	0.023	0.013	0.002	0.003	56.0	913.0	910.0	238.0	5.41	0.0030	15
n.a.	0	20	Blank4	003	25	4	4.5	8.8	1.88	1.25	60	0.63	0.94	0.19	3.13	1.25	0.31	4.38	1.25	0.03	0.563	0.044	0.313	0.035	0.044	0.016	0.003	0.003	33.0	201.0	198.0	80.3	3.43	0.0020	18
n.a.	0	20	Blank5	003	25	4	2.2	4.8	1.31	1.25	0.31	0.63	1.25	0.25	3.13	8.13	0.31	1.88	1.88	0.03	0.438	0.013	0.375	0.087	0.058	0.046	0.001	0.003	348.0	2360.0	2360.0	26.3	7.23	0.0040	20
n.a.	0	20	Blank6	003	25	4	1.8	5.1	1.53	65.3	15.3	10.2	8.57	0.32	1.58	0.61	0.51	2.04	1.02	0.05	0.561	0.051	0.306	0.118	0.026	0.134	0.003	0.005	973.0	6500.0	6500.0	138.0	23.70	0.0170	22
			Median				2.6																						227	1120	1120	138			
			Min				1.8																						33	201	198	26			
			Max				4.5																						973	6500	6500	339			

Table SI-6. Chemical composition of rock samples used for rapid leach tests.
[elemental analysis conducted on ashed samples digested in HCl+HNO3 (partial digestion); MPA, maximum potential acidity; NP, neutralization potential; NNP, net neutralization potential (= NP - MPA); <, less than detection limit]

SAMPLE	LEACH	ROCKTYPE2	MPA	NP	NNP	STOT	Fe	Mn	Al	Si	Ca	Mg	Na	K	Li	Ba	Sr	Zn	Co	Se	Ra226	Ra228	RaTOT	RaRATIO
			g/kg	g/kg	g/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg				
PA1	004	coal	48.1	0.5	-47.6	15400	13000	21	13400	170	2600	381	182	1540	18.4	91.5	118	41.6	7.44	2.66	0.653	0.612	1.27	1.07
PA45	004	coal	34.4	<0.05	-34.35	11000	8720	14.5	19100	245	643	750	405	3470	25	87.5	87	21.8	4.35	0.49	0.685	0.685	1.37	1
PA5	004	coal	76.2	0.26	-75.94	24400	20600	21.9	38100	289	1800	1250	426	5260	36.5	140	138	43.2	10.2	2.17	0.767	1.45	2.22	0.529
BCS3	004	overburden	26.9	7.29	-19.61	8600	77300	1220	121000	558	15600	15700	1760	30200	197	241	61.9	205	30.6	2.03	2.14	2.74	4.88	0.783
HCS	004	overburden	134	0.24	-133.76	42800	53900	317	64800	2230	17600	7420	3990	21300	28.8	68	24.2	305	14.3	8.54	16	1.96	17.9	8.18
KBFWV	004	overburden	12.5	1.6	-10.9	4000	54800	874	91500	4710	5460	10200	4630	28800	47.2	290	70.6	129	19.7	<0.479	1.41	2.81	4.22	0.501
KY1	004	overburden	<0.31	0.17	-0.14	<100	19.9	147	44200	2710	641	135	4150	77.5	<4.91	332	54	30.9	10.4	<0.98	.	.	.	.
KY2	004	overburden	<0.31	3.51	3.2	<100	14.3	322	36100	1800	7860	296	840	57.3	<4.9	235	44.9	23.6	6.49	<0.98	.	.	.	.
KY3	004	overburden	<0.31	1.88	1.57	<100	26	417	61700	2770	3960	393	2210	94.3	<4.82	381	68.9	60.1	13.2	<0.96	.	.	.	.
KY4	004	overburden	0.31	0.43	0.12	100	53.2	350	67800	2180	1070	295	1660	187	<4.81	371	66.9	70	15.7	<0.96	.	.	.	.
KY7	004	overburden	29.4	1.12	-28.28	9400	52300	958	92100	4480	4400	10000	5810	26400	49	183	32.1	151	20.2	<0.5	1.61	2.29	3.89	0.703
KY9	004	overburden	11.6	0.47	-11.13	3700	16800	287	38300	2320	1260	3110	3530	13700	15.5	272	51.4	40.4	7.25	<0.487	0.77	1.3	2.07	0.592
LKFC	004	overburden	29.9	1.36	-28.54	9570	69100	1350	86800	1700	4210	7870	1350	27700	85	43.5	12.7	127	20.3	0.442	1.76	3.1	4.86	0.567
MKSS	004	overburden	9.69	8.66	-1.03	3100	25200	553	66600	1460	14000	5160	1210	20100	26.7	220	42.1	73.6	12.4	<0.978	0.855	1.41	2.26	0.607
TN2	004	overburden	7.5	1.9	-5.6	2400	30100	401	81800	3000	5020	5880	1560	19300	42.8	341	37.5	98.4	15.6	1	1.7	2.57	4.27	0.663
VA16	004	overburden	5	0.77	-4.23	1600	14900	380	35700	2590	2470	2730	422	15700	11.1	234	41.8	35.8	5.44	<0.5	0.531	0.898	1.43	0.591
VA2	004	overburden	14.4	1.59	-12.81	4600	42700	675	84500	3450	3640	7930	1980	24100	49.2	291	58.8	105	16.2	1.07	0.108	0.171	0.279	0.629
VA3	004	overburden	6.25	0.07	-6.18	2000	32700	287	81000	5130	304	5400	2360	23000	53.5	233	48.3	87.2	12.5	<0.5	1.58	2.27	3.85	0.696
VA6	004	overburden	8.44	1.24	-7.2	2700	53500	653	104000	17700	3460	9670	3720	29500	66.9	90.1	16.6	94.3	17	1	1.62	2.46	4.07	0.659
WV5	004	overburden	4.38	2.64	-1.74	1400	25200	493	42200	2040	7360	4890	1660	16200	15.1	309	69	52.9	6.43	<0.486	0.717	1.08	1.8	0.662
PA12	004	refuse	57.8	0.08	-57.72	18500	43500	169	80300	2170	3740	3210	1030	16500	93.4	55.4	17.6	62.1	5.71	3.3	6.11	2.48	8.59	2.46
PA13	004	refuse	65.9	<0.05	-65.85	21100	32700	139	67300	2120	4940	2470	806	11800	63.6	118	75.4	55.9	6.1	2.58	1.75	2.2	3.94	0.795
PA17	004	refuse	188	<0.05	-187.95	60200	65700	36.8	64000	892	1930	2160	738	10700	71.8	120	49.9	52.9	11.6	9.23	1.45	1.99	3.44	0.731
PA22	004	refuse	228	3.86	-224.14	73000	84000	153	39100	542	14400	1770	692	8740	48.5	41.4	30.7	76.3	20.2	10.5	1.16	1.48	2.64	0.786
PA30	004	refuse	244	4.48	-239.52	78100	89500	172	44800	435	20800	2050	641	8830	48.7	107	80.9	87.8	23.5	11.3	1.23	1.47	2.71	0.837
PA31	004	refuse	92.8	0.87	-91.93	29700	48100	275	82000	2280	5640	4450	1230	18800	123	107	74.6	124	24.3	2.08	1.78	2.81	4.58	0.633
PA36	004	refuse	93.4	<0.05	-93.35	29900	53700	185	85600	2890	2750	4160	2110	19300	124	95	50.5	107	15.3	1.94	1.53	2.69	4.22	0.57
PA42	004	refuse	41.6	0.94	-40.66	13300	34000	195	88900	2990	2180	4760	1810	20400	142	46.9	15.4	107	17.8	3.29	1.94	3.17	5.11	0.61
PA48	004	refuse	80.3	<0.05	-80.25	25700	42800	160	96800	2440	4080	4900	1630	19400	133	42.8	27.8	90.6	16.1	1.21	1.96	2.87	4.83	0.682
PA51	004	refuse	41.6	<0.05	-41.55	13300	46600	105	86800	2460	4370	4180	1510	19600	125	38.7	22.1	52.1	6.15	1.52	1.67	3.02	4.69	0.553
PA58	004	refuse	45.3	<0.05	-45.25	14500	41600	147	81600	2540	1350	3710	1380	19300	134	48.2	21.3	70.7	10.6	1.34	1.63	2.81	4.44	0.582
TNR1	004	refuse	25.3	0.54	-24.76	8100	32100	189	99600	7790	1850	6220	1230	23100	89.9	35.2	8.86	99.1	12.6	1.15	2.04	2.74	4.77	0.744
TNR2	004	refuse	33.1	6.49	-26.61	10600	31400	171	81800	2380	14800	4970	1080	20500	130	102	39.5	79.6	12.3	2.54	1.81	2.27	4.09	0.796
TNR3	004	refuse	38.1	0.79	-37.31	12200	38400	246	79700	3270	2200	5870	1700	22400	100	91.5	19.6	112	14.8	2.2	2.02	1.93	3.96	1.04
TGS1	004	refuseU	43.4	0.99	-42.41	13900	32000	175	115000	3600	2100	5750	3260	22900	143	43.6	34.2	137	23.4	2.11	2.47	4.56	7.03	0.542
TGS10A	004	refuseU	208	<0.05	-207.95	66400	98500	41.6	17600	321	569	1190	594	4140	15.2	43.3	47.3	118	92.3	4.44	0.972	0.625	1.6	1.55
TGS10B	004	refuseU	45.9	<0.05	-45.85	14700	27900	71.9	96500	3230	3010	5060	3140	20200	76	60.7	42.2	261	32	2.49	1.74	3.15	4.89	0.554
TGS11	004	refuseU	6.88	0.48	-6.4	2200	10600	31.3	108000	2820	272	2780	3210	15700	145	49.5	21.1	30.3	14.3	6.06	1.91	2.96	4.87	0.644
TGS12	004	refuseU	280	<0.05	-279.95	89600	122000	264	74600	625	22000	4270	3200	16400	30.6	23.1	30.7	73.6	24.4	1.39	3.92	2.34	6.26	1.67
TGS13	004	refuseU	4.06	93.5	89.44	1300	3940	1790	272	1700	145000	2740	102	472	1.53	56.9	268	23.9	1.64	<0.497	1.98	0	1.98	.
TGS14	004	refuseU	216	<0.05	-215.95	69000	97200	212	81000	1290	8470	5400	2630	18900	85.5	40.2	37.9	117	41.2	0.78	1.78	1.85	3.63	0.964
TGS15	004	refuseU	38.4	<0.05	-38.35	12300	21100	67.1	112000	3620	775	4050	3250	20600	93.8	62	29.6	89	16.5	0.66	1.33	0	1.33	.
TGS17	004	refuseU	58.4	15.2	-43.2	18700	31800	318	83000	3900	48400	4920	3970	21500	25.5	297	222	132	21.6	0.49	1.01	2.6	3.61	0.389
TGS2A	004	refuseU	308	<0.05	-307.95	98500	119000	42.5	22700	60	<30.8	587	535	3250	29.3	54.9	39.4	19.5	8.2	0.77	1.02	0.533	1.55	1.91
TGS2B	004	refuseU	39.4	<0.05	-39.35	12600	14900	31.4	97500	2490	362	2660	2420	14600	110	74	42	66.6	16.5	0.44	1.48	2.73	4.21	0.543
TGS3	004	refuseU	47.2	29.8	-17.4	15100	25200	620	47900	3310	89000	4010	3670	17900	13.2	165	299	117	22.7	<0.48	0.838	1.94	2.78	0.431
TGS4	004	refuseU	18.8	1.34	-17.46	6000	42200	685	119000	3370	2260	10100	2640	27900	113	543	178	132	18.7	0.468	1.47	2.95	4.41	0.498
TGS5	004	refuseU	95.6	<0.05	-95.55	30600	19800	18.6	9070	199	1580	281	198	1390	6.32	173	249	16.6	8.26	<0.262	0.329	0.228	0.557	1.45
TGS6	004	refuseU	9.69	0.35	-9.34	3100	10300	32.4	120000	4180	313	3950	3640	19700	193	56	24.5	49.5	6.94	0.91	1.43	3.32	4.76	0.431
TGS7A	004	refuseU	119	18.2	-100.8	38100	45900	250	60700	4050	46300	2640	2800	16700	21.7	127	654	172	26.3	1.04	0.94	2.65	3.59	0.355
TGS7B	004	refuseU	147	0.11	-146.89	46900	39000	41.7	25600	298	4650	1220	657	4720	14.2	363	82.8	65.8	6.44	<0.3	0.569	0.811	1.38	0.701
TGS8	004	refuseU	80	<0.05	-79.95	25600	22300	34.2	26300	263	1980	776	693	4280	28	125	145	.	26.8	0.75	2.2	0.837	3.03	2.62
TGS9	004	refuseU	15.6	0.14	-15.46	5000	8730	16.2	103000	1130	325	1820	2240	10100	139	46	39.5	23.3	12	3.35	3.66	3.86	7.53	0.948
TGS16	004	refuseU	319	0.91	-318.09	12000	145000	134	56400	791	26400	3240	3430	15100	26.6	18.9	55.7	90.5	13.6	0.78	1.6	1.61	3.21	0.994
SKYPA	004	pyrite	117	<0.05	-116.95	37300	44800	11.8	27300	1940	<4.78	1930	169	13300	44.2	115	14.7	68.3	10.9	<0.478	0.362	0.386	0.749	0.938
EGSP01	004	shale	10.9	26.4	15.5	3500	25400	300	72300	6410	113000	8500	3370	23900	42	624	343	66.9	87.8	0.74	.	.	.	.
JKLM01	004	shale	41.9	27.8	-14.1	13400	25700	319	54300	6060	109000	7730	4810	19700	28.4	.	907	110	59.9	1.19	.	.	.	.
JKLM02	004	shale	40.6	27.2	-13.4	13000	25700	316	56800	5270	106000	7890	4910	19900	28.9	.	837	110	60.3	1.29	.	.	.	.
JKLM03	004	shale	45	25	-20	14400	27200	329	58600	5790	97800	8220	5160	20500	29.7	.	805	125	60.7	1.58	.	.	.	.
JKLM04	004	shale	43.4	25.2	-18.2	13900	27400	332	62200	6640	102000	8800	5220	21300	30.9	.	804	130	61.1	1.36	.	.	.	.
JKLM05	004	shale	45.3	23.4	-21.9	14500	27100	315	59100	6650	89200	8460	5270	21400	30.3	.	900	114	64.4	1.34	.	.	.	.

Morris1	004	shale	42.5	39.8	-2.7	13600	19500	267	34800	4580	173000	7960	5180	13600	18.9	6310	2720	63.9	8.96	0.9	.	.	.	.
Morris2	004	shale	43.1	39.7	-3.4	13800	20800	278	36000	4200	175000	8200	5640	14100	19.4	6830	2510	57.9	9.12	1.24	.	.	.	.
Morris3	004	shale	40.6	39.4	-1.2	13000	19400	271	33700	4460	172000	7640	5600	13200	18.2	6870	2300	51.3	8.88	1.49	.	.	.	.
OH01	004	shale	47.8	9.84	-37.96	15300	49400	616	76200	4210	25800	13000	5100	29600	58	416	159	114	85.5	0.74	.	.	.	.

Table SI-10. Summary of field chemistry and leachate results for the 10 paired field sites.
L1 (deionized water), and L3 (30% H2O2+10% CO2).

Analyte		MA_F	MA_L1	MA_L3	MB_F	MB_L1	MB_L3	SK_F	SK_L1	SK_L3	MP_F	MP_L1	MP_L3	BCS3_F	BCS3_L1	BCS3_L3	LKFC_F	LKFC_L1	LKFC_L3	KY1_F	KY1_L1	KY1_L3	KY2_F	KY2_L1	KY2_L3	KY3_F	KY3_L1	KY3_L3	KY9_F	KY9_L1	KY9_L3
SC	Mean	8,110	2,350	6,060	8,240	2,180	8,170	21,100	5,480	25,900	11,400	6,270	12,900	1,680	1,510	2,750	1,520	2,270	5,750	644	141	464	777	106	687	828	324	1,670	1,630	1,010	3,390
µS/cm	Max	13,500	3,180	10,100	14,000	2,880	12,700	30,300	7,140	28,500	13,000	31,100	31,900	3,590	1,510	2,750	3,980	2,270	5,750	2,160	326	471	2,110	115	710	2,560	341	1,770	2,770	1,010	3,390
	Min	3,820	1,640	2,100	2,520	1,190	5,010	11,700	4,060	21,200	9,690	340	1,350	633	1,510	2,750	495	2,270	5,750	91.0	47.0	455	323	91.0	651	308	312	1,550	265	1,010	3,390
pH	Mean	3.6	4.1	2.3	3.6	4.4	2.1	2.2	2.8	1.3	6.8	4.6	3.1	5.59	7.50	6.70	4.30	5.00	2.10	7.7	6.8	3.4	8.1	7.7	7.0	8.0	7.2	6.5	NP	6.9	2.7
	Max	5.8	6.2	3.3	7.2	6.8	2.5	2.3	2.9	1.5	7.6	7.6	7.5	7.51	7.50	6.70	7.04	5.00	2.10	9.3	7.0	3.4	8.8	7.8	7.5	8.7	7.3	6.5	NP	6.9	2.7
	Min	2.5	2.6	1.8	2.7	2.9	1.7	2.0	2.7	1.2	6.3	2.2	1.3	2.95	7.50	6.70	2.70	5.00	2.10	5.6	6.7	3.3	7.0	7.6	6.3	6.7	7.0	6.4	NP	6.9	2.7
Ca	Mean	NP	364	401	NP	295	463	NP	56.3	248.1	0.32	136	308	154	254	527	110	270	377	50.3	3.26	39.4	39.5	7.91	69.9	56.5	26.1	218	NP	113	383
mg/L	Max	NP	446	501	NP	410	526	NP	56.3	248.1	0.41	491	563	410	254	527	380	270	377	277	3.26	39.4	178	7.91	69.9	345	26.1	218	NP	113	383
	Min	NP	234	121	NP	42.5	398	NP	56.3	248.1	0.15	1.88	8.13	46.0	254	527	48.0	270	377	7.26	3.26	39.4	4.38	7.91	69.9	8.63	26.1	218	NP	113	383
Mg	Mean	NP	30.1	67.9	NP	72.5	111	NP	27.5	36.3	168	58.6	83.4	49.0	59.0	130	49.0	184	328	28.9	1.71	15.2	40.7	4.37	28.1	46.6	13.6	99.5	NP	53.8	178
mg/L	Max	NP	55.6	99.4	NP	144	197	NP	27.5	36.3	242	230	246	104	59.0	130	210	184	328	164	1.71	15.2	219	4.37	28.1	189.6	13.6	99.5	NP	53.8	178
	Min	NP	15.0	16.9	NP	3.75	53.8	NP	27.5	36.3	35.0	0.313	3.13	16.0	59.0	130	13.0	184	328	1.20	1.71	15.2	6.67	4.37	28.1	6.52	13.6	99.5	NP	53.8	178
Na	Mean	NP	3.50	4.50	NP	51.0	82.1	NP	0.625	6.250	2,270	275	359	92.0	8.75	6.25	18.0	9.38	3.75	13.6	1.71	2.98	7.82	1.16	1.46	9.38	1.46	1.93	NP	3.13	5.00
mg/L	Max	NP	5.00	9.38	NP	188	284	NP	0.625	6.250	2,660	731	756	460	8.75	6.25	112	9.38	3.75	54.4	1.71	2.98	40.4	1.16	1.46	43.6	1.46	1.93	NP	3.13	5.00
	Min	NP	1.88	1.25	NP	1.88	1.25	NP	0.625	6.250	2,030	6.88	21.9	2.60	8.75	6.25	1.00	9.38	3.75	0.400	1.71	2.98	0.540	1.16	1.46	0.590	1.46	1.93	NP	3.13	5.00
K	Mean	NP	2.88	2.88	NP	4.69	9.27	NP	1.88	12.50	25.9	12.4	25.2	5.01	8.54	14.7	3.35	9.58	3.75	NP	1.71	5.36	NP	3.68	6.27	NP	7.74	15.0	NP	12.5	26.9
mg/L	Max	NP	5.00	6.88	NP	12.5	35.0	NP	1.88	12.50	54.6	29.2	86.3	12.0	8.54	14.7	9.60	9.58	3.75	NP	1.71	5.36	NP	3.68	6.27	NP	7.74	15.0	NP	12.5	26.9
	Min	NP	1.25	1.25	NP	1.25	1.25	NP	1.88	12.50	11.2	1.25	1.25	2.00	8.54	14.7	1.00	9.58	3.75	NP	1.71	5.36	NP	3.68	6.27	NP	7.74	15.0	NP	12.5	26.9
Fe	Mean	969	190	971	1,160	49.3	1,390	9,525	863	5860	352	3,260	5,380	59.5	0.31	6.53	87.9	2.31	778	0.900	0.152	3.83	0.169	0.290	0.230	0.131	0.314	0.321	NP	0.188	132
mg/L	Max	2,180	788	1,690	3,470	119	2,590	18,200	863	5860	590	32,300	29,600	164	0.31	6.53	512	2.31	778	3.81	0.152	3.83	0.480	0.290	0.230	0.340	0.314	0.321	NP	0.188	132
	Min	20.9	5.25	66.3	11.4	0.125	466	1,850	863	5860	2.26	0.125	0.250	0.102	0.31	6.53	0.160	2.31	778	0.040	0.152	3.83	0.020	0.290	0.230	0.010	0.314	0.321	NP	0.188	132
Al	Mean	43.1	32.0	69.9	168	36.3	164	3,670	535	781	0.721	201	280	6.97	0.38	1.41	17.0	0.419	76.3	Np	0.569	23.6	NP	0.580	0.627	NP	0.63	2.65	NP	0.313	20.0
mg/L	Max	117	80.6	162	511	77.5	251	6,430	535	781	2.03	1,300	1,491	58.8	0.38	1.41	100	0.419	76.3	NP	0.569	23.6	NP	0.580	0.627	NP	0.63	2.65	NP	0.313	20.0
	Min	4.37	0.313	3.13	3.21	0.313	47.5	1,190	535	781	0.033	0.313	0.313	0.013	0.38	1.41	0.011	0.419	76.3	NP	0.569	23.6	NP	0.580	0.627	NP	0.63	2.65	NP	0.313	20.0
Mn	Mean	20.0	4.80	12.5	40.6	9.07	19.9	234	0.438	0.750	5.13	2.76	6.03	5.11	0.39	31.2	6.69	27.3	93.1	0.100	0.091	9.27	0.060	0.044	0.617	0.077	0.036	22.2	NP	1.44	29.9
mg/L	Max	53.3	11.3	22.1	64.0	20.5	31.9	444	0.438	0.750	9.67	10.50	21.38	20.4	0.39	31.2	45.0	27.3	93.1	0.650	0.091	9.27	0.310	0.044	0.617	0.460	0.036	22.2	NP	1.44	29.9
	Min	6.37	1.63	1.06	3.14	0.044	7.38	44.0	0.438	0.750	0.590	0.013	0.038	0.213	0.39	31.2	0.120	27.3	93.1	0.010	0,.091	9.27	0.010	0.044	0.617	0.010	0.036	22.2	NP	1.44	29.9
SO_4	Mean	5,040	1,220	2,680	8,450	1,230	4,130	57,300	2,850	17,100	4,920	4,890	10,220	819	829	1,680	754	1,420	2,940	162	7.85	24.2	125	4.18	20.1	155	88.1	2,000	NP	563	1320
mg/L	Max	9,840	1,870	4,310	26,300	1,730	6,690	97,600	2,850	17,100	8,130	52,400	56,100	1,900	829	1,680	2,000	1,420	2,940	995	7.85	24.2	875	4.18	20.1	1,340	88.1	2,000	NP	563	1320
	Min	1,820	675	969	1,670	488	1,960	20,900	2,850	17,100	1,860	3.13	344	260	829	1,680	120	1,420	2,940	4.92	7.85	24.2	7.92	4.18	20.1	4.71	88.1	2,000	NP	563	1320
HCO_3	Mean	NP	2.27	0.006	NP	19.8	0.003	NP	0.007	0.001	NP	31.0	73.2	NP	64.2	137	NP	0.462	0.004	NP	22.7	0.028	NP	27.1	53.6	NP	22.7	12.9	NP	21.0	0.010
mg/L	Max	NP	9.81	0.022	NP	82.3	0.006	NP	0.007	0.001	NP	228	540	NP	64.2	137	NP	0.462	0.004	NP	22.7	0.028	NP	27.1	53.6	NP	22.7	12.9	NP	21.0	0.010
	Min	NP	0.003	0.001	NP	0.007	0.002	NP	0.007	0.001	NP	0.003	0.001	NP	64.2	137	NP	0.462	0.004	NP	22.7	0.028	NP	27.1	53.6	NP	22.7	12.9	NP	21.0	0.010
Cl	Mean	NP	5.38	2.63	NP	7.63	4.00	NP	5.63	9.38	1,370	22.2	25.0	18.2	4.58	30.31	5.52	1.88	13.8	2.60	1.71	50.8	2.67	1.35	70.4	2.53	1.67	2.50	NP	2.50	NP
mg/L	Max	NP	11.9	5.00	NP	15.6	6.88	NP	5.63	9.38	2,020	101	75.6	62.6	4.58	30.31	30.4	1.88	13.8	13.7	1.71	50.8	22.7	1.35	70.4	28.2	1.67	2.50	NP	2.50	NP
	Min	NP	2.50	1.25	NP	5.00	1.88	NP	5.63	9.38	397	2.50	3.75	1.90	4.58	30.31	0.400	1.88	13.8	0.240	1.71	50.8	0.070	1.35	70.4	0.160	1.67	2.50	NP	2.50	NP

Field site	Rock samples	Field measurements	Ref
Mine A	Weathered refuse n=5	Field sampling + DEP reports n =42	n.p.
Mine B	Weathered refuse n=6	Field sampling + DEP reports n =41	n.p.
Mines P	Unweathered refuse n=17	Field sampling n=3	1
KY1	Weathered overburden n=1	Automated SC meter n=189	
KY2	Unweathered overburden n=1	Automated SC meter n=100	2
KY3	Weathered overburden n=1	Automated SC meter n=199	
KY9	Mixed overburden n=1	Automated SC meter n=18,064	n.p.
LKFC	Unweathered overburden n=1	Field sampling n=27	1,3
BCS3	Unweathered overburden n=1	Field sampling n=16	1,3
Skytop	Pyrite n=1	Field sampling n=4	4

1 – Cravotta and Brady (2015) Applied Geochemistry 62, 108-130

2 – Sena et al. (2014) Water, Air and Soil Pollution 225, 1-14
3 – Cravottta (2008) Applied Geochemistry 23, 166-202
n.p. – not yet published

Table SI-11. Spearman rank correlation coefficient (r) matrix for XRD, acid-base account parameters, and leachate chemistry
[r-values multiplied by 100 and rounded; only values significant at α = 0.001 shown]

LEACH001+002+003	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
	NPppt	MPAppt	NNPppt	MPANPppt	FeSulfide	FeSulfate	Gypsum	Carbonate	Sminl	CO3Sminl	SC25lab	KScalc	SC25phrq	TDSphrq	OSMPphrqm	pH	TIC	ALK	NALK	NACID	SO4	Fe	Ca	Mg
1 NPppt	100	-32	54			-50		74		37	-40	-26	-40	-48	-28	76	58	79	71	-71	-54	-68		-29
2 MPAppt	-32	100	-92	91	63	32			71	47	62	44	62	66	59	-46	-29	-45	-54	54	63	54	41	25
3 NNPppt	54	-92	100	-75	-42	-35	-27	27	-58		-62	-47	-62	-69	-55	61	44	61	66	-66	-70	-65	-34	-36
4 MPANPppt		91	-75	100	67				66	56	54	42	55	57	55	-33		-29	-44	44	52	46	43	
5 FeSulfide		63	-42	67	100			32	61	62					28									
6 FeSulfate	-50	32	-35			100		-29	40		39		38	41	32	-43		-45	-48	48	42	47		
7 Gypsum			-27				100		37														41	33
8 Carbonate	74		27		32	-29		100		74				-25		59	48	62	49	-49	-33	-51		
9 Sminl		71	-58	66	61	40	37		100	75	46		46	48	42	-32		-32	-39	39	42	35	46	
10 CO3Sminl	37	47		56	62			74	75	100													44	
11 SC25lab	-40	62	-62	54		39			46		100	78	98	97	97	-65		-63	-72	72	94	65	61	63
12 KScalc	-26	44	-47	42							78	100	78	75	77	-56		-52	-53	53	72	49	48	46
13 SC25phrq	-40	62	-62	55		38			46		98	78	100	98	97	-70		-65	-76	76	94	69	62	62
14 TDSphrq	-48	66	-69	57		41		-25	48		97	75	98	100	93	-74	-30	-70	-82	82	98	75	63	67
15 OSMPphrq	-28	59	-55	55	28	32			42		97	77	97	93	100	-57		-53	-64	64	88	60	57	54
16 pH	76	-46	61	-33		-43		59	-32		-65	-56	-70	-74	-57	100	46	91	91	-91	-77	-88	-27	-48
17 TIC	58	-29	44					48						-30		46	100	65	42	-42	-34	-43		
18 ALK	79	-45	61	-29		-45		62	-32		-63	-52	-65	-70	-53	91	65	100	85	-85	-72	-84		-43
19 NALK	71	-54	66	-44		-48		49	-39		-72	-53	-76	-82	-64	91	42	85	100	-100	-84	-95	-36	-57
20 NACID	-71	54	-66	44		48		-49	39		72	53	76	82	64	-91	-42	-85	-100	100	84	95	36	57
21 SO4	-54	63	-70	52		42		-33	42		94	72	94	98	88	-77	-34	-72	-84	84	100	78	59	69
22 Fe	-68	54	-65	46		47		-51	35		65	49	69	75	60	-88	-43	-84	-95	95	78	100	25	42
23 Ca		41	-34	43			41		46	44	61	48	62	63	57	-27			-36	36	59	25	100	67
24 Mg	-29	25	-36				33				63	46	62	67	54	-48		-43	-57	57	69	42	67	100

LEACH001	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
	NPppt	MPAppt	NNPppt	MPANPppt	FeSulfide	FeSulfate	Gypsum	Carbonate	Sminl	CO3Sminl	SC25lab	KScalc	SC25phrq	TDSphrq	OSMPphrqm	pH	TIC	ALK	NALK	NACID	SO4	Fe	Ca	Mg
1 NPppt	100		54			-50		76		43	-45		-44	-54		81	68	84	71	-71	-66	-68		-44
2 MPAppt		100	-91	91	61				71	44	71	56	73	74	67	-57		-49	-58	58	66	55	57	
3 NNPppt	54	-91	100	-75					-55		-74	-58	-75	-80	-64	70	45	64	69	-69	-80	-64	-59	-49
4 MPANPppt		91	-75	100	67				65	54	60	52	63	62	61	-41			-48	48	51	47	50	
5 FeSulfide		61		67	100				62	64														
6 FeSulfate	-50					100					45		46	46		-53		-52	-52	52	47	50		
7 Gypsum							100																60	
8 Carbonate	76							100		77						60	58	67	44	-44	-43	-48		
9 Sminl		71	-55	65	62				100	74	49		54	51	49				-43	43			57	
10 CO3Sminl	43	44		54	64			77	74	100														
11 SC25lab	-45	71	-74	60		45			49		100	75	99	97	95	-68		-62	-65	65	88	55	69	67
12 KScalc		56	-58	52							75	100	72	70	71	-44		-42			61		50	49
13 SC25phrq	-44	73	-75	63		46			54		99	72	100	98	96	-69		-62	-68	68	89	56	71	68
14 TDSphrq	-54	74	-80	62		46			51		97	70	98	100	90	-77	-44	-68	-76	76	95	66	72	72
15 OSMPphrqm		67	-64	61					49		95	71	96	90	100	-56		-48	-52	52	77	43	56	52
16 pH	81	-57	70	-41		-53		60			-68	-44	-69	-77	-56	100	65	88	87	-87	-84	-81	-44	-57
17 TIC	68		45					58						-44		65	100	86	55	-55	-47	-54		
18 ALK	84	-49	64			-52		67			-62	-42	-62	-68	-48	88	86	100	79	-79	-73	-75		-51
19 NALK	71	-58	69	-48		-52		44	-43		-65		-68	-76	-52	87	55	79	100	-100	-82	-90	-51	-61
20 NACID	-71	58	-69	48		52		-44	43		65		68	76	52	-87	-55	-79	-100	100	82	90	51	61
21 SO4	-66	66	-80	51		47		-43			88	61	89	95	77	-84	-47	-73	-82	82	100	74	65	75
22 Fe	-68	55	-64	47		50		-48			55		56	66	43	-81	-54	-75	-90	90	74	100		43
23 Ca		57	-59	50			60		57		69	50	71	72	56	-44			-51	51	65		100	79
24 Mg	-44		-49								67	49	68	72	52	-57		-51	-61	61	75	43	79	100

LEACH003	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24

XRD-ABA-leachate correlation matrix. Significant Spearman (rank) correlation coefficients are shown for rock leaches 001, 002, and 003, combined (excluding blanks), in the first table and, then, separately for leaches 001 and 003. Each correlation matrix includes acid-base-accounting, XRD, and selected leachate chemistry parameters. For quantification of XRD, sulfur and carbonate minerals were assigned values of 2 (major), 1 (minor), or 0 (not identified).

The overall correlation matrix and charts support the hypothesis that samples containing sulfide and sulfate minerals (Sminl; FeSulfide; FeSulfate) have higher total sulfur content and corresponding potential for acid formation (expressed MPAppt = S% x 31.25) . Likewise, samples containing Calcite and Dolomite (Carbonate) have higher neutralization potential (NP) than other rock types/samples.

The samples containing sulfur minerals generate the highest conductivity and associated measures of salinity.

Also, the computed net alkalinity (negative of net acidity) for the leaches, combined, is correlated with the net neutralization potential (NP-MPA) and is positively correlated with samples containing carbonate minerals and negatively correlated with those containing FeSulfate minerals. The strongest correlations between ABA parameters and net alkalinity are indicated for leach 003.

The salinity (SPC, TDS, or osmotic pressure) of the leaches is not significantly correlated to the sum of MPA+NP (MPANPppt). The strongest predictor of salinity is the total sulfur (MPAppt) concentration and the presence of sulfur minerals (Sminl).

The correlations considering only leaches 001 or 003 support the hypothesis that leach 001 liberates sulfur and iron mainly from FeSulfate minerals (slightly higher coefficients than those for leach 003). Identification of FeSulfide does not seem to be particularly informative for predicting water chemistry. Generally, the significance of correlations between ABA parameters and salinity parameters increases for leach 003 (which seems to mobilize Ca from carbonates, whereas leach 001 mobilizes Ca from gypsum).

		NPppt	MPAppt	NNPppt	MPANPppt	FeSulfide	FeSulfate	Gypsum	Carbonate	SminI	CO3SminI	SC25lab	KScalc	SC25phrq	TDSphrq	OSMPphrqm	pH	TIC	ALK	NALK	NACID	SO4	Fe	Ca	Mg
1	NPppt	100		54			-50		76		43	-54	-44	-61	-59	-46	84	61	87	82	-82	-62	-78	46	
2	MPAppt		100	-91	91	61				71	44	74	52	77	77	76	-50	-45	-57	-55	55	76	60		
3	NNPppt	54	-91	100	-75					-55		-76	-60	-80	-82	-74	69	62	76	72	-72	-83	-75		
4	MPANPppt		91	-75	100	67				65	54	63	45	66	65	68				-42	42	63	49	48	
5	FeSulfide		61		67	100				62	64													45	
6	FeSulfate	-50					100					44		48	45	44			-45	-49	49	46	48		
7	Gypsum							100																	
8	Carbonate	76							100		77			-44	-46		70	48	69	68	-68	-49	-67	57	
9	SminI		71	-55	65	62				100	74	57		58	56	58						52		47	
10	CO3SminI	43	44		54	64			77	74	100													68	
11	SC25lab	-54	74	-76	63		44			57		100	73	96	92	96	-68	-42	-77	-70	70	90	70		
12	KScalc	-44	52	-60	45							73	100	75	70	69	-62		-62	-59	59	71	61		
13	SC25phrq	-61	77	-80	66		48		-44	58		96	75	100	98	96	-78	-49	-83	-81	81	97	82		
14	TDSphrq	-59	77	-82	65		45		-46	56		92	70	98	100	93	-78	-55	-83	-83	83	99	84		46
15	OSMPphrq	-46	76	-74	68		44			58		96	69	96	93	100	-63		-70	-67	67	91	68		
16	pH	84	-50	69					70			-68	-62	-78	-78	-63	100	62	95	95	-95	-80	-94		
17	TIC	61	-45	62					48			-42		-49	-55		62	100	71	66	-66	-58	-64		
18	ALK	87	-57	76			-45		69			-77	-62	-83	-83	-70	95	71	100	94	-94	-84	-92		
19	NALK	82	-55	72	-42		-49		68			-70	-59	-81	-83	-67	95	66	94	100	-100	-85	-98		
20	NACID	-82	55	-72	42		49		-68			70	59	81	83	67	-95	-66	-94	-100	100	85	98		
21	SO4	-62	76	-83	63		46		-49	52		90	71	97	99	91	-80	-58	-84	-85	85	100	86		47
22	Fe	-78	60	-75	49		48		-67			70	61	82	84	68	-94	-64	-92	-98	98	86	100		
23	Ca	46			48	45			57	47	68													100	
24	Mg														46							47			100

Abbre- viat	Mineral name	Name for: Mineral-	
	1	Group, Sub- group or S	Speciesor compo- nent
Act	Actinolite	0	1
Aeg	Aegirine	0	1
Agt	Aegirine-augite	0	1
Ak	Åkermanite (Akermanite)	0	1
Ab	Albite	0	1
Afs	Alkalifeldspar	1	0
Aln	Allanite	1	0
Alm	Almandine	0	1
Als	Alumosilicate	1	0
Am	Amphibole	1	0
Anl	Analcime	0	1
Ant	Anatase	0	1
And	Andalusite	0	1
Adr	Andradite	0	1
Anh	Anhydrite	0	1
Ank	Ankerite	0	1
Ann	Annite	0	1
An	Anorthite	0	1
Ath	Anthophyllite	0	1
Atg	Antigorite	0	1
Ap	Apatite	1	0
Apo	Apophyllite	1	0
Arg	Aragonite	1	1
Arf	Arfvedsonite	0	1
Apy	Arsenopyrite	1	1
Aug	Augite	0	1
Ax	Axinite	1	0
Brt	Barite	1	1
Brs	Barroisite	0	1
Brl	Beryl	1	1
Bt	Biotite	1	0
Bhm	Böhmite (Boehmite)	0	1
Bn	Bornite	0	1
Brk	Brookite	0	1
Brc	Brucite	1	1
Bst	Bustamite	0	1
Cal	Calcite	1	1
Ccn	Cancrinite	1	1
Cb	Carbonate mineral	1	0
Cph	Carpholite	1	1
Cst	Cassiterite	0	1
Cel	Celadonite	0	1
Cls	Celestine	0	1
Cbz	Chabazite	1	0
Cc	Chalcocite	0	1

Ccp	Chalcopyrite	1	1
Chm	Chamosite	0	1
Chl	Chlorite	1	0
Cld	Chloritoid	0	1
Chn	Chondrodite	0	1
Chr	Chromite	0	1
Ccl	Chrysocolla	0	1
Ctl	Chrysotile	1	0
Cam	Clinoamphibole	1	0
Clc	Clinochlore	0	1
Cen	Clinoenstatite	0	1
Fe2-Chq	Clinoferroholmquistite	0	1
Cfs	Clinoferrosilite	0	1
Chq	Clinoholmquistite	0	1
Chu	Clinohumite	0	1
Cpx	Clinopyroxene	1	0
Czo	Clinozoisite	0	1
Coe	Coesite	0	1
Crd	Cordierite	0	1
Crn	Corundum	0	1
Cv	Covellite	0	1
Crs	Cristobalite	0	1
Cum	Cummingtonite	0	1
Dee	Deerite	0	1
Dsp	Diaspore	0	1
Dg	Digenite	0	1
Di	Diopside	0	1
Dol	Dolomite	1	1
Drv	Dravite	0	1
Eck	Eckermannite	0	1
Ed	Edenite	0	1
Elb	Elbaite	0	1
En	Enstatite	0	1
Ep	Epidote	1	1
Fa	Fayalite	0	1
Fsp	Feldspar	1	0
Fe2-Act	Ferro-Actinolite	0	1
Fe2-Ed	Ferro-Edenite	0	1
Fe2-Hbl	Ferrohornblende	0	1
Fs	Ferrosilite	0	1
Fe2-Ts	Ferrotschermakite	0	1
Fl	Fluorite	0	1
Fo	Forsterite	0	1
Gad	Gadolinite	1	0
Gn	Galena	1	1
Grt	Garnet	1	0
Ged	Gedrite	0	1

Gh	Gehlenite	0	1
Gbs	Gibbsite	0	1
Glt	Glauconite	0	1
Gln	Glaucophane	0	1
Gt	Goethite	0	1
Gr	Graphite	0	1
Gre	Greenalite	0	1
Grs	Grossular	0	1
Gru	Grunerite	0	1
Gp	Gypsum	0	1
Hem	Haematite (Hematite)	1	1
Hl	Halite	1	1
Hs	Hastingsite	0	1
Hyn	Haüyne	0	1
Hd	Hedenbergite	0	1
Hc	Hercynite	0	1
Hul	Heulandite	1	0
Hgb	Högbomite (Hoegbomite)	1	0
Hq	Holmquistite	0	1
Hbl	Hornblende	1	0
Hu	Humite	1	1
Ill	Illite	1	0
Ilm	Ilmenite	1	1
Jd	Jadeite	0	1
Joe	Joesmithite	0	1
Jh	Johannsenite	0	1
Krs	Kaersutite	0	1
Kls	Kalsilite	0	1
Kln	Kaolinite	0	1
Kln-Srp	Kaolinite-Serpentine	1	0
Ktp	Katophorite	0	1
Kfs	K-feldspar	1	0
Kie	Kieserite	1	1
Krn	Kornerupine	0	1
Koz	Kôzulite (Kozulite)	0	1
Ky	Kyanite	0	1
Lmt	Laumontite	0	1
Lws	Lawsonite	1	1
Laz	Lazulite	1	1
Lpd	Lepidolite	1	0
Lct	Leucite	0	1
Lm	Limonite	1	0
Lz	Lizardite	0	1
Lo	Löllingite(Loellingite)	1	1
Mgh	Maghemite	0	1
Mg-Hbl	Magnesiohornblende	0	1
Mg-Ktp	Magnesiokatophorite	0	1

Mg-Rbk	Magnesioriebeckite	0	1
Mg-Sdg	Magnesiosadanagaite	0	1
Mgs	Magnesite	0	1
Mag	Magnetite	0	1
Mrc	Marcasite	1	1
Mrg	Margarite	0	1
Mar	Marialite	0	1
Mei	Meionite	0	1
Mel	Melilite	1	1
Mw	Merwinite	0	1
Mca	Mica	1	0
Mc	Microcline	0	1
Mns	Minnesotaite	0	1
Mo	Molybdenite	0	1
Mnz	Monazite	1	0
Mtc	Monticellite	0	1
Mnt	Montmorillonite	0	1
Mul	Mullite	0	1
Ms	Muscovite	0	1
Ntr	Natrolite	0	1
Ne	Nepheline	0	1
Nrb	Norbergite	0	1
Nsn	Nosean	0	1
Nyb	Nyböite (Nyboeite)	0	1
Ol	Olivine	1	0
Omp	Omphacite	0	1
Op	Opaque mineral	1	0
Oam	Orthoamphibole	1	0
Or	Orthoclase	0	1
Opx	Orthopyroxene	1	0
Osu	Osumilite	1	1
Pg	Paragonite	0	1
Prg	Pargasite	0	1
Pct	Pectolite	0	1
Pn	Pentlandite	1	1
Per	Periclase	1	1
Prv	Perovskite	1	1
Phg	Phengite	1	0
Phl	Phlogopite	0	1
Pgt	Pigeonite	0	1
Pl	Plagioclase	1	0
KMg-Sdg	Potassic- Magnesiosadanagaite	0	1
K-Sdg	Potassicsadanagaite	0	1
Prh	Prehnite	0	1
Pmp	Pumpellyite	1	0
Py	Pyrite	1	1
Pcl	Pyrochlore	1	1

Prp	Pyrope	0	1
Prl	Pyrophyllite	0	1
Prl-Tlc	Pyrophyllite-Talc	1	0
Px	Pyroxene	1	0
Po	Pyrrhotite	0	1
Qtz	Quartz	0	1
Rds	Rhodochrosite	0	1
Rdn	Rhodonite	0	1
Rit	Richterite	0	1
Rbk	Riebeckite	0	1
Rt	Rutile	1	1
Sdg	Sadanagaite	1	0
Sa	Sanidine	0	1
Spr	Sapphirine	0	1
Scp	Scapolite	1	0
Srl	Schorl	0	1
Sep	Sepiolite	0	1
Ser	Sericite	1	0
Srp	Serpentine	1	0
Sd	Siderite	0	1
Sil	Sillimanite	0	1
Sme	Smectite	1	0
Sdl	Sodalite	1	1
Sps	Spessartine	0	1
Sp	Sphalerite	1	1
Spl	Spinel	1	1
Spd	Spodumene	0	1
St	Staurolite	1	1
Stb	Stilbite	1	0
Stp	Stilpnomelane	0	1
Stv	Stishovite	0	1
Str	Strontianite	0	1
Tlc	Talc	0	1
Tmt	Taramite	0	1
Ttn	Titanite	1	1
Toz	Topaz	0	1
Tur	Tourmaline	1	0
Tr	Tremolite	0	1
Trd	Tridymite	0	1
Tro	Troilite	0	1
Ts	Tschermakite	0	1
Usp	Ulvöspinel (Ulvoespinel)	0	1
Uvt	Uvarovite	0	1
Vrm	Vermiculite	1	0
Ves	Vesuvianite	0	1
Viv	Vivianite	1	1
Wrk	Wairakite	0	1

Wmca	White Mica	1	0
Win	Winchite	0	1
Wth	Witherite	0	1
Wo	Wollastonite	1	1
Wus	Wüstite (Wuestite)	0	1
Xtm	Xenotime	1	0
Zeo	Zeolite	1	0
Zwd	Zinnwaldite	1	0
Zrn	Zircon	1	1
Zo	Zoisite	0	1