Applied Geochemistry 91 (2018) 97–106

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Mineralogical influences on water quality from weathering of surface coal mine spoils

Elyse V. Clark[a,*], W. Lee Daniels[a], Carl E. Zipper[a], Kenneth Eriksson[b]

[a] *Department of Crop and Soil Environmental Sciences, 185 Ag Quad Lane, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061, USA*
[b] *Department of Geosciences, 926 West Campus Drive, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061, USA*

ARTICLE INFO

Handling Editor: A. Kolker

Keywords:
Total dissolved solids
Column leaching
Acid-base accounting
Geochemistry

ABSTRACT

Surface coal mining fractures geologic materials to access coal seams. The excavated rock materials (mine spoils) have freshly exposed mineral surfaces that weather rapidly and release soluble ions to streams during and after site reclamation. The soluble ion release is directly influenced by the mine spoil mineralogy. We examined relationships among mine spoil mineralogical and geochemical properties and soluble ion release for the purpose of determining their influence on Appalachian stream water quality. We determined the mineralogy, bulk spoil composition, leachate concentrations, and acid-base accounting (ABA) parameters of 16 non-acid-forming spoil samples. Mineralogical composition was determined using thin section spectroscopy, a column leaching experiment was conducted to determine eluted leachate concentrations of 15 elements, and ABA parameters were determined using conventional methodologies. Results indicated that the mine spoils were comprised predominantly of quartz, with smaller amounts of plagioclase and K-feldspars, lithic metamorphic fragments, muscovite, chlorite, and goethite. Cementing agents included quartz, kaolinite, siderite, and carbonate. Indicators of weathering observed in samples presumed to be unweathered included halloysite at the expense of feldspar and goethite at the expense of pyrite and siderite. On an oxide basis, SiO_2 and Al_2O_3 dominated the bulk geochemical composition. Sulfate had the largest initial leachate concentration whereas HCO_3^- was the dominant anion in final leachates. The ABA tests indicated most spoils were non-acid-forming, with total sulfur values ranging from 0.01 to 0.38%. Relatively high dissolved sulfate elution was attributed to trace pyrites. Carbonates were not observed in many samples, indicating other mineral sources neutralized the acid produced by pyrite oxidation. Feldspar hydrolysis and the weathering of metamorphic lithic fragments (schists), chlorite, and muscovite may have been responsible, in part, for soluble ion release and acid-neutralization. Bulk Mg contents often exceeded Ca for most samples, and high Mg:Ca ratios in leachate concentrations relative to regional waters may be attributed to chlorite weathering. Historically, high levels of soluble ion release was assumed to be controlled by sulfide oxidation reactions coupled with carbonate neutralization reactions. These results, however, indicate that other minerals typically presumed to be relatively stable also contribute significantly to overall soluble ion release in this highly disturbed environment. Minimizing the amount of time water is in contact with mine spoils and, by extension, decreasing the potentials for chemical weathering, may assist with controlling soluble ion discharges from Appalachian coal mining areas.

1. Introduction

Appalachian surface coal mining disturbs large volumes of geologic materials by blasting the strata above coal seams into fractured rock, termed “mine spoils”. Under the Surface Mining Control and Reclamation Act (SMCRA, 1977), mine spoils are used to reconstruct landforms to their approximate pre-mining contour, and excess materials after landform reconstruction are typically placed into the heads of valleys as V-shaped landforms called valley fills (VFs; Griffith et al., 2012). This type of mining has disturbed > 6000 km^2 of land in the Appalachians since the 1970's (Zipper et al., 2011) and is ongoing today.

Fracturing previously buried geologic strata exposes those materials to surficial weathering while increasing reactive surface areas. When water and oxygen come into contact with the freshly fractured and exposed mineral surfaces, chemical weathering is initiated and water-soluble ions are released. The typical ions released from Appalachian coal mine spoils via weathering include Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^- in

---

[*] Corresponding author. Present Address: Department of Geology and Environmental Earth Science, Miami University, Oxford, OH, 45056, USA.
E-mail address: clarkev@miamioh.edu (E.V. Clark).

https://doi.org/10.1016/j.apgeochem.2018.02.001
Received 4 August 2017; Received in revised form 29 January 2018; Accepted 1 February 2018

relatively high concentrations, and other major and trace ions (Hartman et al., 2005; Griffith et al., 2012). Collectively, these ions constitute total dissolved solids (TDS) and are typically characterized in streams using the proxy specific conductance (SC). Elevated TDS/SC (SC frequently $> 1000\ \mu S\ cm^{-1}$) has been documented in Appalachian coal mining-influenced streams (Hartman et al., 2005; Pond et al., 2008, 2014; Evans et al., 2014), as well as other streams influenced by mining activities globally in areas including Australia, Germany, Ghana, Nigeria, and Norway (Søndergaard et al., 2007; Acheampong et al., 2013; Ezekwe et al., 2013; Alhamed and Wohnlich, 2014; Singh et al., 2016; Ali et al., 2017). In Appalachian streams draining relatively undisturbed watersheds, SCs are generally $< 100\ \mu S\ cm^{-1}$ and nearly always $< 200\ \mu S\ cm^{-1}$ (Pond et al., 2008, 2014; Timpano et al., 2015). Elevated TDS/SC in Appalachia has been associated with losses of certain aquatic taxa at SCs $> 300–500\ \mu S\ cm^{-1}$ (Pond et al., 2008; Cormier et al., 2013), and these impacts commonly occur with circumneutral to moderately alkaline discharges rather than the low pH acid mine drainage conditions that were of concern historically (Herlihy et al., 1990).

Under SMCRA, mining firms are required to pre-test rock materials for their potential to produce acidity and neutralize acid production. This testing enables mining companies to select strata that have the lowest potentials for influencing water quality via acid generation. Results of those tests are used to select strata for placement into VFs, where there are high potentials for water-rock interaction. The test commonly used for this purpose is acid-base accounting (ABA), which predicts if strata are potentially acid-producing or acid-neutralizing (Sobek et al., 2000; Skousen et al., 2002). The ABA first analyzes for total S, which is used to predict the maximum potential acidity (MPA) which is then summed against and neutralization potential (NP), in order to determine the net neutralization potential (NNP) of individual strata. Total S is conservatively assumed to include only reactive pyritic-S forms. If strata have strongly negative NNP values (> 5 Mg calcium carbonate equivalent acid demand/1000 Mg spoil), they are considered likely to be acid-generating and are isolated away from hydrologic flows. Conversely, strata with positive NNP values and/or ratios of NP/MPA > 2.0 are typically acid-neutralizing, and may be used as topsoil substitutes for reclamation or placed in areas with high water-rock contact potentials (Skousen et al., 2002).

Mine spoil mineralogies and mechanisms of geochemical weathering responsible for acid generation are well known (e.g. Blowes et al., 2014). In contrast, geochemical weathering mechanisms for release of major ions and trace elements comprising TDS/SC in circumneutral to alkaline mine drainages, and for releases from mine spoil minerals generally considered unreactive, are not well documented. Since spoil mineralogical properties directly influence the potential for release of bulk TDS, it is important to better understand the effects of spoil mineralogy on TDS release in non-acid forming mine spoils. Specific objectives of this study were to: (1) Determine the petrography of Appalachian non-acid-forming coal mining overburden samples; (2) Describe the mineralogical composition of those overburden samples; and (3) Determine the relationship of mineralogy to bulk spoil geochemical composition, elemental release via leaching, and ABA parameters of these mine spoils. We hypothesized that samples with higher proportions of easily weatherable minerals would also have greater release of elements during leaching and larger NP values, indicating higher ion release.

2. Background and methodology

2.1. Geologic setting

Coals in the central Appalachian basin formed during the Pennsylvanian Period, as the closure of the Rheic Ocean and Appalachian Orogeny resulted in transgressive and regressive sequences (Quinlan and Beaumont, 1984; Martino, 2016). During that period the central Appalachian basin was located close to the equator and drifting north, with fluvial systems draining to an inland sea in the west (Arkle, 1974; Rosenau et al., 2013). Many transgressive and regressive sequences occurred, likely due to tectonically-induced subsidence enabling space for sediment accumulation (Klein and Willard, 1989) or to sea level fluctuations (Aitken and Flint, 1994; Martino, 1996), resulting in the deposition of sand, silt, and mud that formed the coal-bearing stratigraphic units in central Appalachia.

Central Appalachian coal-bearing stratigraphic units are comprised primarily of sandstones, siltstones, and shales that differ mineralogically. A prior study of Central Appalachian coal-bearing strata in Fayette County, West Virginia based on core sampling found that sandstones had a mineralogical composition consisting of ~60% quartz, ~15% feldspars, ~10% kaolinite, 1–2% dolomite, and < 1% of pyrite, siderite, chlorite, and illite (Dulong et al., 1997). Comparatively, siltstones had ~45% quartz, ~10% feldspars, ~15% kaolinite, 2–3% chlorite, 1–2% pyrite and dolomite, and < 1% siderite and illite. Lastly, shales were comprised of ~30% quartz, ~10% feldspars, ~20% kaolinite, ~4% chlorite, 1–2% pyrite and siderite, and < 1% dolomite and illite. Calcite was rare (< 0.4%) to not present in most samples and rock types above the first coal seam. Sandstones, siltstones, and shales above the first coal seam in the Fayette County core samples tended to have sulfur values ranging from ~0.01 to 0.5% (Dulong et al., 1997). Mineralogy and ion release potentials are also influenced by rock weathering status, which is influenced directly by proximity to the land surface (Daniels et al., 2016).

Prior studies have correlated the Pennsylvanian-aged coal-bearing stratigraphic units in the central Appalachian basin (e.g. Greb et al., 2008). Of interest in this study is the Wise Formation of Virginia, the Allegheny and Kanawha Formations of southern West Virginia, and the Princess and Four Corners Formations of eastern Kentucky; all formations are middle-Pennsylvanian aged (Fig. 1) and are considered parts of the Pottsville and Allegheny groups (USGS, 2012). The Wise and Kanawha formations of Virginia and West Virginia, respectively, are considered time equivalent, whereas the Allegheny and Princess

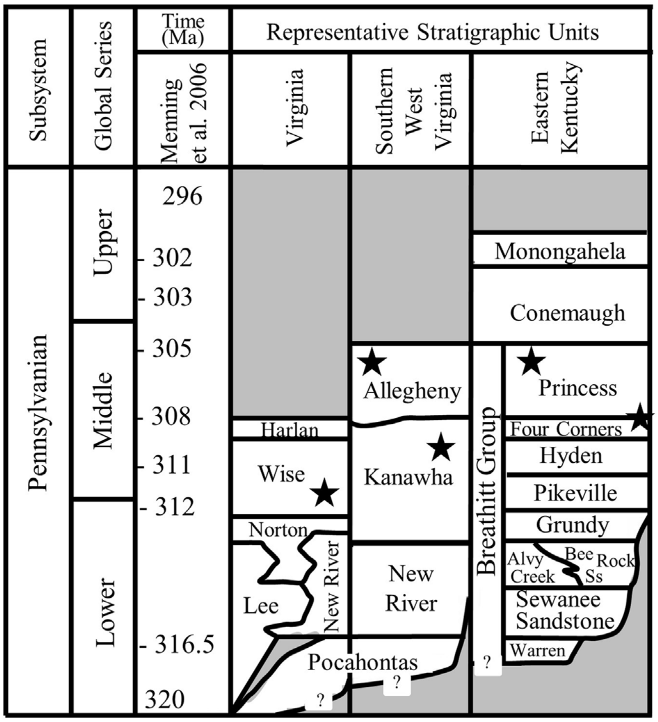

Fig. 1. Stratigraphy of the Central Appalachian coalfields of southwestern Virginia, southern West Virginia, and eastern Kentucky. Rock samples were collected from the formations with stars. Figure based on Greb et al. (2008).