



Geochemical modeling to understand and mitigate aquatic contamination by abandoned mine drainage

Charles A. Cravotta III

Cravotta Geochemical Consulting, Bethel, PA, USA, cravottageochemical@gmail.com,
ORCID 0000-0003-3116-4684

Extended Abstract

Abandoned mine drainage (AMD) from legacy coal mines degrades thousands of kilometers of streams across the northern Appalachian Coal Basin of eastern USA. Where it emerges to the surface, AMD generally has field-measured pH that is acidic (2.5-4) or near-neutral (pH 6-7) (Fig. 1) along with elevated concentrations of CO_2 , SO_4 , Fe, Al, Mn, and other constituents (Cravotta and Kirby, 2004; Kirby and Cravotta, 2005a, 2005b; Cravotta, 2008a, 2008b; Vesper et al., 2016; Vass et al., 2019a, 2019b). Although the pH of net-acidic AMD tends to decrease after discharging, net-alkaline AMD has sufficient alkalinity to maintain $\text{pH} \geq 6$ after outgassing of CO_2 and complete oxidation of Fe and Mn (Fig. 1). Nevertheless, because atmospheric equilibration and oxidation can be slow compared to travel time, even net-alkaline AMD can be a long-term source of stream contamination by Fe, Mn, and SO_4 (Cravotta, 2015; Cravotta et al., 2014, 2015; Cravotta and Brady, 2015). Thus, to mitigate negative effects on the aquatic environment, net-acidic or net-alkaline AMD could warrant treatment to meet mine effluent limits ($\text{pH} 6-9$, Fe < 7 mg/L, Mn < 5 mg/L) or in-stream criteria ($\text{pH} 6-9$, Fe < 1.5 mg/L, Mn < 1 mg/L) (Commonwealth of Pennsylvania, 2020).

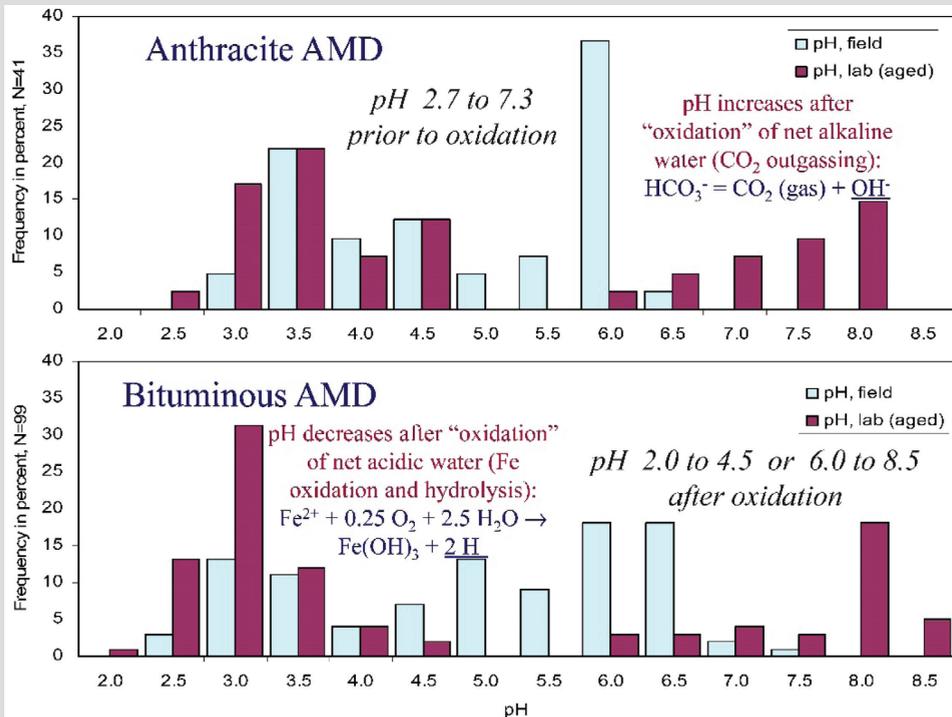


Figure 1 Bimodal pH of 140 abandoned mine drainage sample (adapted from Cravotta and Kirby, 2004; Kirby and Cravotta, 2005b). Outgassing of CO_2 causes pH of aged samples to increase, while Fe oxidation and hydrolysis cause pH to decrease.

Although treatment of net-alkaline AMD may simply require aeration/decarbonation and sufficient retention time to facilitate Fe oxidation and settling of metal-rich particles, treatment of net-acidic AMD also requires alkalinity addition. Various passive and/or active treatment strategies may be appropriate depending on the AMD flow and chemistry, site characteristics, funding, and operational logistics plus the chemical and biological characteristics of the receiving water body (Cravotta and Brady, 2015; Skousen et al., 2017, 2019).

In general, AMD treatment promotes an increase in the pH or Fe oxidation state with consequent increases in the potential to (1) precipitate relatively soluble Fe^{II} (and Mn^{II}) phases and/or (2) oxidize Fe and precipitate lower solubility Fe^{III} phases (Fig. 2). Because of relatively high solubility of Fe^{II} phases at near-neutral pH (Fig. 2), oxidation is needed to effectively decrease dissolved Fe concentrations and loadings to streams (Cravotta et al., 2014, 2015; Cravotta, 2021). The precipitated Fe^{III} oxyhydroxides may adsorb and effectively attenuate concentrations of Mn^{II} and various trace elements at near-neutral pH (Cravotta, 2008a, 2008b, 2021, 2022; Cravotta and Brady, 2015). Thus, if near-neutral pH is maintained and stream habitat is suitable, recovery of fish populations and other aquatic life in historically mining impaired watersheds may be anticipated (Cravotta et al., 2010).

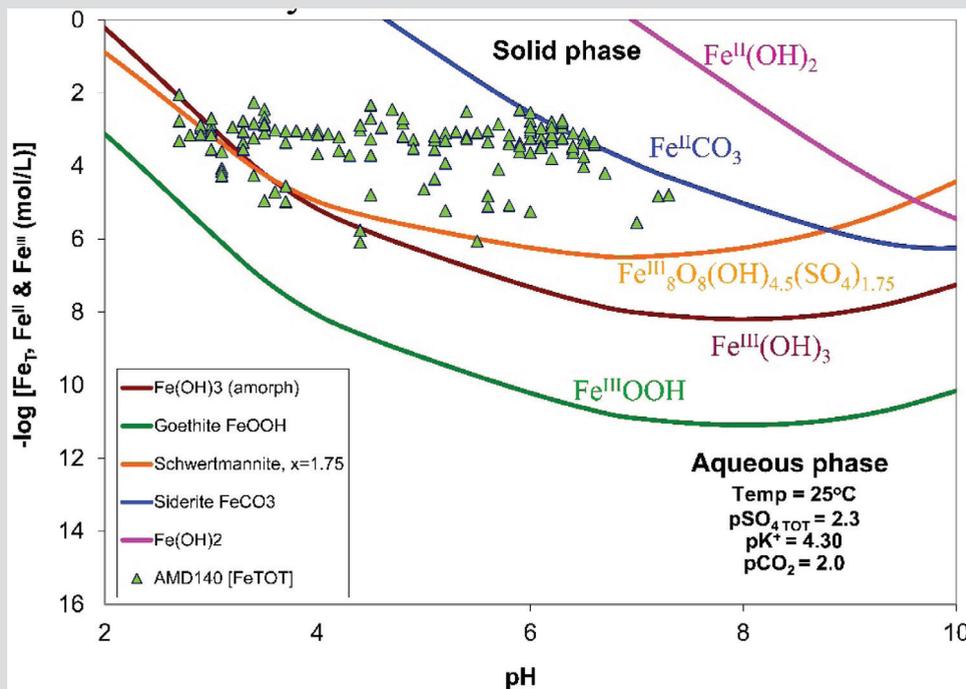


Figure 2 Total dissolved Fe concentrations for 140 AMD samples relative to equilibrium conditions for siderite ($\text{Fe}^{\text{II}}\text{CO}_3$), amorphous $\text{Fe}^{\text{III}}(\text{OH})_3$, goethite ($\text{Fe}^{\text{III}}\text{OOH}$), schwertmannite ($\text{Fe}^{\text{III}}_8\text{O}_8(\text{OH})_{4.5}(\text{SO}_4)_{1.75}$), and jarosite ($\text{KFe}^{\text{III}}_3(\text{SO}_4)_2(\text{OH})_6$) (adapted from Kirby and Cravotta, 2005a; Cravotta, 2008b). Fe^{III} phases may limit Fe concentrations in low-pH samples; however, Fe^{II} is the predominant Fe oxidation state for most AMD samples. Siderite equilibrium could limit dissolved Fe concentrations for net-alkaline AMD at $\text{pH} \geq 6$

Eventually, AMD treatment may not be warranted to meet effluent discharge limits or in-stream thresholds for aquatic life, because AMD sources invariably become less acidic over a decadal timeframe with progressively decreasing concentrations of

contaminants (Younger, 2000; Demchak et al., 2004; Mack and Skousen, 2008; Raymond and Oh, 2009; Burrows et al., 2014; Schaffer et al., 2023, 2024a). As the water quality evolves to become less contaminated, adjustments to AMD management strategies and funding estimates may be warranted. For example, considering the water-quality evolution model for a large underground coal mine, shown in Fig. 3, net-acidic AMD during the first and second decades (0–20 years) may require active treatment with a caustic chemical, whereas marginally net-alkaline quality during the third and fourth decades (20–40 years) could involve peroxide treatment without alkaline additives (e.g. Means et al., 2013), transitioning to passive aeration thereafter (40–100 years) (e.g. Cravotta, 2007; Hedin, 2008; Skousen et al., 2017). The selected treatment technologies consider the water-quality characteristics plus the cost-effectiveness and feasibility for implementation of treatment, explained in more detail below.

The rate of AMD evolution, especially the timing of transition from net-acidic to net-alkaline character, and projection of long-term water-quality trends are difficult to predict. Nevertheless, future projections of the pH, net acidity, Fe, SO₄, and other solute concentrations may be constrained by site-specific hydrological information, such as the background groundwater composition and recharge rate, and geochemical observations, such as mineralogy and aqueous equilibrium conditions (e.g. Schaffer et al., 2023, 2024a).

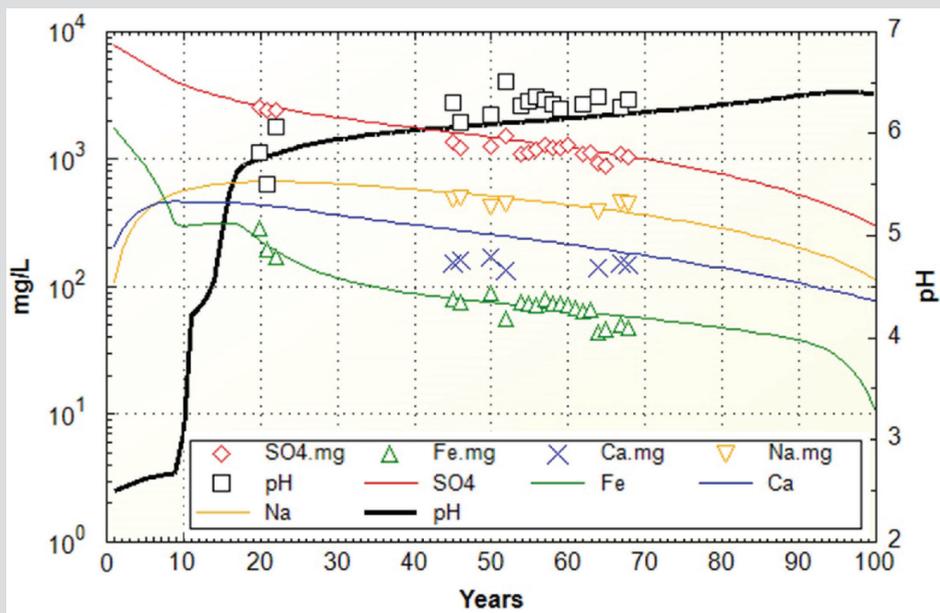


Figure 3 Novel “first-flush” hydrogeochemical evolution model that incorporates groundwater dilution and geochemical reactions over decadal timeframe, for Lowber Mine, southwestern Pennsylvania (adapted from Schaffer et al., 2023, 2024a, 2024b). Simulated (lines) and measured (points) values for SO₄, Fe, Ca, and Na (mg/L) and pH are shown for the model scenario considering constant groundwater influx combined with progressively decreasing mineral dissolution and cation exchange. The timing for transition from net-acidic to net-alkaline character is indicated by the change in pH from <4 to >5.5. At any time, concentration of Fe is limited by equilibrium with jarosite, schwertmannite, amorphous Fe(OH)₃, and/or siderite

Because of uncertainty in predictions, effective solutions to AMD problems at a given site may necessitate study and experiments to understand interactions and primary variables that influence the chemistry of the untreated and treated AMD. For example, various studies have been published on mineralogical composition and likely water-rock interactions to explain post-mining groundwater quality (Cravotta, 1991, 1994; Cravotta et al., 1994a, 1994b; Schaffer et al., 2024a). Additional studies focused on factors affecting the rates of important reactions in proposed or constructed AMD treatment systems, including kinetics models of limestone dissolution (Cravotta and Trahan, 1998; Cravotta, 2003, 2008c; Cravotta et al., 2008) and of CO₂ outgassing and Fe oxidation (Geroni et al., 2012; Cravotta, 2007, 2015, 2021). Such studies and resultant understanding of important environmental factors have been considered for development of geochemical models to explain and integrate spatial and temporal variations in AMD quality at watershed to site scales (e.g. Cravotta et al., 2014; Schaffer et al., 2024a) as well as those within AMD-impaired streams and AMD treatment facilities (Cravotta et al., 2015; Cravotta, 2020, 2021, 2022).

PHREEQ-N-AMDTreat is a new water-quality modeling tool, based on the “TreatTrainMix2” model developed by Cravotta (2020, 2021), that uses PHREEQC (Parkhurst and Appelo, 2013) to simulate changes in water quality during passive or active treatment. This tool was recently incorporated with the newly recoded AMDTreat 6.0 Beta treatment cost-analysis model (Office of Surface Mining Reclamation and Enforcement, 2022). By adjusting kinetic variables or chemical dosing, effects of independent or sequential treatment steps that have different retention time, aeration rate, or quantities of reactive solids can be assessed for a specified influent. When considered with the AMDTreat 6.0 cost-analysis model, the tool may be applied to evaluate long-term management strategies. Importantly, based on modeled reaction time estimates for successive treatment steps, which correspond to the system size, the AMDTreat cost-analysis model may be used to estimate long-term funding requirements for treatment system installation plus recapitalization and annual operations and maintenance. Thus, various active and/or passive treatment strategies and associated liability can be identified for initial, current, or future effluent. For the case illustrated in Fig. 3 and explained in detail by Schaffer et al. (2024b), the liability for active treatment during 0-20 years, expressed as net-present value, was estimated to exceed \$30 million USD, whereas that for passive treatment after 40 years, decreased to less than \$10 million USD. Although timing and long-term predictions of water-quality changes are imprecise, such analysis clearly demonstrates the importance of geochemical modeling for understanding, planning, and mitigating aquatic contamination by AMD. The modeling may be used to indicate cost-effectiveness of various treatment scenarios and guide empirical testing to corroborate model estimates and to refine treatment designs.

Keywords: Aqueous speciation, saturation indices, bimodal pH, equilibrium, kinetics, AMDTreat, PHREEQC

Acknowledgements

The author, who retired from the U.S. Geological Survey (USGS) in December 2023, is grateful to organisers for hosting the IMWA2023 Conference and to former and current colleagues at the USGS, the Office of Surface Mining Reclamation and Enforcement, the Pennsylvania Department of Environmental Protection, and various universities that offered opportunities for collaboration

and continued learning. This contribution was conceived as a review of relevant research by the author, initially for an invited presentation at the 2023 National Meeting of the Geological Society of America in Pittsburgh, PA <https://gsa.confex.com/gsa/2023AM/meetingapp.cgi/Paper/391408>. Although the original abstract was approved by the USGS for publication, this extended version has not been subjected to USGS review and approval steps.

References

- Burrows JE, Peters SC, Cravotta CA III (2015) Temporal geochemical variations in above- and below-drainage coal mine discharge. *Appl Geochem* 62:84-95. <https://doi.org/10.1016/j.apgeochem.2015.02.010>
- Commonwealth of Pennsylvania (2020) 25 Pa. Code Chapter 93. Water Quality Standards. Table 3. https://www.pacodeandbulletin.gov/secure/pacode/data/025/chapter93/025_0093.pdf
- Cravotta CA III (1991) Geochemical evolution of acidic ground water at a reclaimed surface coal mine in western Pennsylvania, in Proceedings of the 1991 National Meeting of the American Society for Surface Mining and Reclamation, Durango, Co. American Soc Surface Mining Reclam 43-68. <https://doi.org/10.21000/JASMR91010043>
- Cravotta CA III (1994) Secondary iron-sulfate minerals as sources of sulfate and acidity: The geochemical evolution of acidic ground water at a reclaimed surface coal mine in Pennsylvania, in Alpers CN and Blowes DW, eds., Environmental geochemistry of sulfide oxidation. Washington, D.C., American Chemical Society Symposium Series 550:345-364. <http://pubs.acs.org/doi/pdf/10.1021/bk-1994-0550.ch023>
- Cravotta CA III (2003) Size and performance of anoxic limestone drains to neutralize acidic mine drainage. *J Environ Qual* 32:1277-1289. <https://doi.org/10.2134/jeq2003.1277>
- Cravotta CA III (2007) Passive aerobic treatment of net-alkaline, iron-laden drainage from a flooded underground anthracite mine, Pennsylvania, USA: *Mine Water Environ* 26:128-149. <https://doi.org/10.1007/s10230-007-0002-8>
- Cravotta CA III (2008a) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA — 1. Constituent concentrations and correlations. *Appl Geochem* 23:166-202. <https://dx.doi.org/10.1016/j.apgeochem.2007.10.011>
- Cravotta CA III (2008b) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA — 2. Geochemical controls on constituent concentrations. *Appl Geochem* 23:203-226. <https://dx.doi.org/10.1016/j.apgeochem.2007.10.003>
- Cravotta CA III (2008c) Laboratory and field evaluation of a flushable oxic limestone drain for treatment of net-acidic drainage from a flooded anthracite mine, Pennsylvania, USA. *Appl Geochem* 23:3404-3422. <https://doi.org/10.1016/j.apgeochem.2008.07.015>
- Cravotta CA III (2015) Monitoring, field experiments, and geochemical modeling of Fe(II) oxidation kinetics in a stream dominated by net-alkaline coal-mine drainage, Pennsylvania, USA. *Appl Geochem* 62:96-107. <http://dx.doi.org/10.1016/j.apgeochem.2015.02.009>
- Cravotta CA III (2020) Interactive PHREEQ-N-AMDTreat water-quality modeling tools to evaluate performance and design of treatment systems for acid mine drainage (software download). US Geol Surv Software Release <https://doi.org/10.5066/P9QEE3D5>
- Cravotta CA III (2021) Interactive PHREEQ-N-AMDTreat water-quality modeling tools to evaluate performance and design of treatment systems for acid mine drainage. *Appl Geochem* 126:104845. <https://doi.org/10.1016/j.apgeochem.2020.104845>
- Cravotta CA III (2022) Interactive PHREEQ-N-AMDTreat+REYS water-quality modeling tools to evaluate potential attenuation of rare-earth elements and associated dissolved constituents by aqueous-solid equilibrium processes (software download). US Geol Surv Software Release. <https://doi.org/10.5066/P9M5QVK0>
- Cravotta CA III, Brady KBC (2015) Priority pollutants and associated constituents in untreated and treated discharges from coal mines in Pennsylvania, U.S.A. *Appl Geochem* 62:108-130. <https://doi.org/10.1016/j.apgeochem.2015.03.001>
- Cravotta CA III, Kirby CS (2004) Acidity and alkalinity in mine drainage--practical considerations, in 2004 National Meeting of the American Society of Mining and Reclamation. American Soc Mining Reclam 334-365. <https://doi.org/10.21000/JASMR04010334>
- Cravotta CA III, Trahan MK (1999) Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. *Appl Geochem* 14:581-606. [https://doi.org/10.1016/S0883-2927\(98\)00066-3](https://doi.org/10.1016/S0883-2927(98)00066-3)
- Cravotta CA III, Brady KBC, Gustafson-Minnich LC, DiMatteo MR (1994a) Geochemical and geohydrological characteristics of bedrock and mine spoil from two methods of mining at a reclaimed surface coal mine in Clarion County, PA, USA: US Bur Mines Special Pub

- SP 06B, p. 242-249. <https://doi.org/10.21000/JASMR94020242>
- Cravotta CA III, Dugas DL, Brady KBC, Kovalchuk TE (1994b) Effects of selective handling of pyritic, acid-forming materials on the chemistry of pore gas and ground water at a reclaimed surface coal mine in Clarion County, PA, USA. US Bur Mines Special Pub SP 06A, 365-374. <https://doi.org/10.21000/JASMR94010365>
- Cravotta CA III, Ward SJ, Hammarstrom JM (2008) Downflow limestone beds for treatment of net-acidic, oxic, iron-laden drainage from a flooded anthracite mine, Pennsylvania, USA—Laboratory evaluation. *Mine Water Environ* 27:86–99. <https://doi.org/10.1007/s10230-008-0031-y>
- Cravotta CA III, Brightbill RA, Languard MJ (2010) Abandoned mine drainage in the Swatara Creek Basin, Southern Anthracite Coalfield, Pennsylvania, USA—1. Streamwater-quality trends coinciding with the return of fish. *Mine Water Environ* 29:176-199. <https://doi.org/10.1007/s10230-010-0112-6>
- Cravotta CA III, Goode DJ, Bartles MD, Risser DW, Galeone DG (2014) Surface-water and groundwater interactions in an extensively mined watershed, upper Schuylkill River, Pennsylvania, USA. *Hydrol Processes* 28:3574–3601. <https://doi.org/10.1002/hyp.9885>
- Cravotta CA III, Means B, Arthur W, McKenzie R, Parkhurst DL (2015) AMDTreat 5.0+ with PHREEQC titration module to compute caustic chemical quantity, effluent quality, and sludge volume. *Mine Water Environ* 34:136–152. <https://doi.org/10.1007/s10230-014-0292-6>
- Demchak J, Skousen J, McDonald LM (2004) Longevity of acid discharges from underground mines located above the regional water table. *J Environ Qual* 33:656-668. <https://doi.org/10.2134/jeq2004.0656>
- Geroni JN, Cravotta CA III, Sapsford DJ (2012) Evolution of the chemistry of Fe bearing waters during CO₂ degassing. *Appl Geochem* 27:2335-2347 <https://doi.org/10.1016/j.apgeochem.2012.07.017>
- Hedin RS (2008) Iron removal by a passive system treating alkaline coal mine drainage. *Mine Water Environ* 27:200–209. <https://doi.org/10.1007/s10230-008-0041-9>
- Kirby CS, Cravotta CA III (2005a) Net alkalinity and net acidity 1: Theoretical considerations. *Appl Geochem* 20:1920-1940. <http://dx.doi.org/10.1016/j.apgeochem.2005.07.002>
- Kirby CS, Cravotta CA III (2005b) Net alkalinity and net acidity 2: Practical considerations. *Appl Geochem* 20:1941-1964. <http://dx.doi.org/10.1016/j.apgeochem.2005.07.003>
- Mack B, Skousen J (2008) Acidity decay curves of 40 above drainage mines in West Virginia. *Proc Am Soc Min Reclam* 612-627. <http://dx.doi.org/10.21000/JASMR08010612>
- Means B, Beam R, Charlton D (2013) Operational and financial studies of hydrogen peroxide versus hydrated lime and hydrogen peroxide versus sodium hydroxide at two Pennsylvania mine drainage treatment sites. 2013 West Virginia Mine Drainage Task Force Symposium. <https://wvmdtaskforce.files.wordpress.com/2016/01/13-means-paper.doc>
- Office of Surface Mining Reclamation and Enforcement (2022) AMDTreat 6.0 Beta. <https://www.osmre.gov/programs/reclaiming-abandoned-mine-lands/amdtreat>
- Parkhurst DL, Appelo CAJ (2013) Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *US Geol Surv Tech Methods* 6-A43. <https://doi.org/10.3133/tm6A43>
- Raymond PA, Oh N-H (2009) Long term changes of chemical weathering products in rivers heavily impacted from acid mine drainage: Insights on the impact of coal mining on regional and global carbon and sulfur budgets. *Earth Planet Sci Lett* 284:50-56. <https://doi.org/10.1016/j.epsl.2009.04.006>
- Schaffer CR, Cravotta CA, Capo RC, Stewart BW, Hedin BC, Vesper DJ (2023). Quantifying and predicting long-term evolution of coal mine drainage in a Pittsburgh coal basin: Geological Society of America Abstracts with Programs, v. 55, no. 6, <https://doi.org/10.1130/abs/2023AM-392263>
- Schaffer CR, Cravotta CA, Capo RC, Hedin BC, Vesper DJ, Stewart BW (2024a) Multi-decadal geochemical evolution of coal mine drainage in an Appalachian coal basin. *Sci Total Environ* (in revision)
- Schaffer CR, Cravotta CA, Capo RC, Stewart BW, Hedin BC, Vesper DJ (2024b) Coal mine drainage contaminant trend prediction in an

- Appalachian basin, USA. 2024 West Virginia Mine Drainage Task Force Symposium & 15th International Mine Water Association Congress (this proceedings).
- Skousen JG, Zipper CE, Rose AW, Ziemkiewicz PF, Nairn R, McDonald LM, Kleinmann RL (2017) Review of passive systems for acid mine drainage treatment. *Mine Water Environ* 36, 133–153. <https://doi.org/10.1007/s10230-016-0417-1>
- Skousen JG, Ziemkiewicz PF, McDonald LM (2019) Acid mine drainage formation, control and treatment: Approaches and strategies. *Extr Ind Soc* 6:241–249. <https://doi.org/10.1016/J.EXIS.2018.09.008>
- Vass CR, Noble A, Ziemkiewicz PF (2019a) The occurrence and concentration of rare earth elements in acid mine drainage and treatment byproducts: Part 1 – Initial survey of the northern Appalachian coal basin. *Mining Metal Explor* 36:903-916. <https://doi.org/10.1007/s42461-019-0097-z>
- Vass CR, Noble A, Ziekiewicz P (2019b) The occurrence and concentration of rare earth elements in acid mine drainage and treatment byproducts. Part 2—regional survey of northern and central Appalachian coal basins. *Mining Metal Explor* 36:917-929. <https://doi.org/10.1007/s42461-019-00112-9>
- Vesper DJ, Moore JE, Adams JP (2016) Inorganic carbon dynamics and CO₂ flux associated with coal-mine drainage sites in Blythedale PA and Lambert WV, USA. *Environ Earth Sci* 75(4):340. <https://doi.org/10.1007/s12665-015-5191-z>
- Younger PL (2000) Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: a first approximation. *J Contam Hydrol* 44:47-69. [https://doi.org/10.1016/S0169-7722\(00\)00090-5](https://doi.org/10.1016/S0169-7722(00)00090-5)