



# Coal mine drainage contaminant trend prediction in an Appalachian basin, USA

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## Abstract

Underground coal mine drainage chemistry typically improves over a decadal timeframe after its initial formation; however, site-specific hydrogeochemical processes complicate accurate prediction of contaminant reduction and treatment strategy decisions. Progressive evolution of the first-flush drainage composition is simulated with a geochemical evolution model using PHREEQC. The net-acidic to net-alkaline transition results from progressive groundwater dilution plus sustained water-mineral reactions involving carbonate minerals and cation-exchange by clays. Various treatment strategies and costs were evaluated with AMDTreat 6.0 software: initial flush, early net-alkaline, present-day alkaline, and future. Over time, implementation of passive technologies resulted in decreased costs and improved water quality.

**Keywords:** Coal mine drainage, geochemistry, first-flush, predictive model, contaminant trends

## Introduction

Coal mine drainage (CMD) in Northern Appalachia, United States, is a major pollutant that impairs thousands of kilometers of waterways with acidic, sulfate-rich, metalliferous effluent for decades after mine abandonment. Underground CMD geochemistry generally improves over a decadal timeframe, and deep minepool CMD often transitions from a net-acidic to net-alkaline character (Wood 1996; Younger 1997; Burrows et al. 2015). Regionally and globally, major contaminant concentration trends in deep mines follow a 'first-flush' behaviour (Younger 1997; Merritt and Power 2022). During mining operations, pyrite oxidation products, including various acid-sulfate salts, accumulate in the humid minevoid and overlying dewatered strata (Cravotta 1994). After mine abandonment and flooding, contaminant concentrations

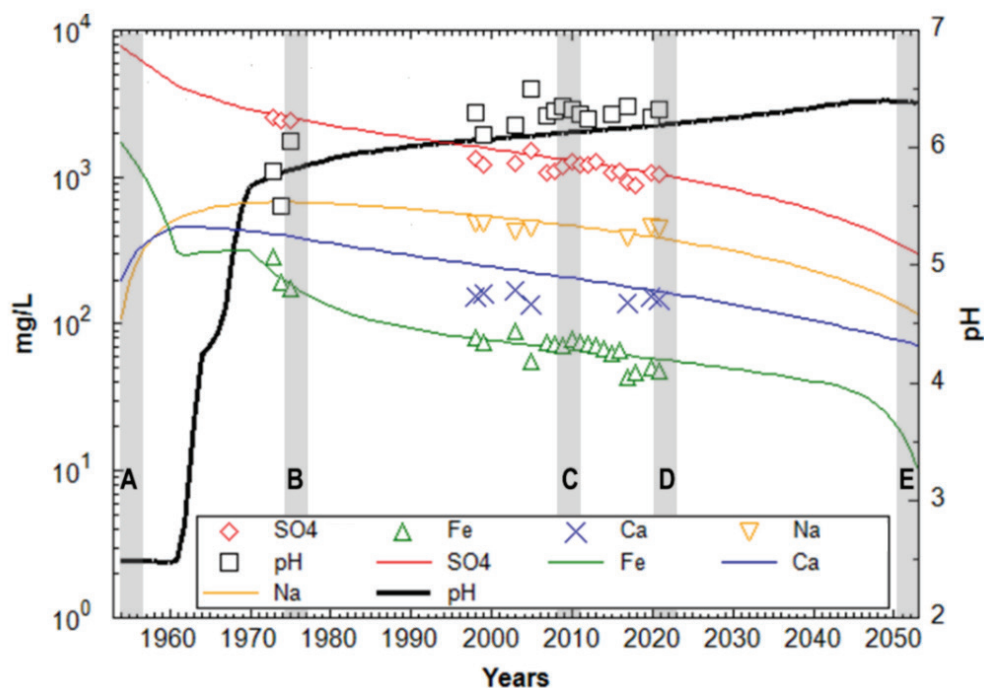
initially peak as secondary oxidation products readily dissolve; this is followed by a rapid, exponential decline, and eventual approach to steady-state behaviour (Younger 1997; Merritt and Power 2022). However, CMD chemistry is variable, and the rate of chemical improvement is difficult to predict because of spatial and temporal hydrological variability and non-linear water-rock interactions.

Models that consider complex hydrogeochemical factors are needed to predict the evolution of mine effluent chemistry. A mixing and reaction model of the first flush followed by contaminant decline was developed using PHREEQC (Parkhurst and Appelo 2013, Schaffer et al. 2023, 2024). The model simulates the net-acidic to net-alkaline evolution of an Appalachian CMD discharge (Lowber, western Pennsylvania) for 100 years following mine closure, from the initial minepool flooding in 1953. Rather

than simply fitting exponential functions to observed data, multiple physical and chemical processes are considered to explain observations and estimate trends. Progressive groundwater dilution of an acidic, highly mineralized first-flush solution by ambient groundwater plus water-mineral reactions involving pyrite, carbonates (calcite, dolomite, siderite), and cation-exchange by clays (illite, chlorite, mixed layer illite/smectite) were modelled to explain the temporal contaminant trends and transition to Na-rich, net-alkaline water (fig. 1). The processes are simulated to occur throughout time, considering realistic constraints such as mixing ratio of groundwater (residence time), eventual consumption of reactant phases, and anticipated mineral equilibrium conditions.

Flow, net-acidity, metals, and dissolved oxygen concentrations are critical factors in determining appropriate treatment

technologies (Skousen et al. 2017, 2019). Long-term treatment strategies may be optimized by using predicted values for future CMD contaminant concentrations and trends. For years to decades after mine abandonment, Appalachian CMD can be very acidic (pH < 3) with elevated concentrations of  $\text{SO}_4$ , Fe, Al, Mn, and other metals. This can require costly, active treatment strategies, such as those that continuously aerate and dose CMD with caustic chemicals and flocculants. However, as the mine water chemistry evolves to net-alkaline character, some components of treatment may be scaled back and/or transitioned to more economically favourable options. For example, in active treatment technologies, a switch from hydrated lime to hydrogen peroxide is a cheaper, alternative chemical (Means et al. 2013). Likewise, long-term decreases in Fe and other metals loading can translate to reducing the system size or



**Figure 1** Forward mixing and reaction model results of the Lowber discharge from the first flush to 100 years after closure (adapted from Schaffer et al. 2023, 2024). Simulated (lines) and measured (points) concentrations of major contaminants (Fe and  $\text{SO}_4$ , mg/L), cations (Na and Ca, mg/L) and pH are shown. Grey shaded regions, referred to as periods A-E, represent different chemical conditions warranting different treatment strategies, modelled with PHREEQ-N-AMDTreat in AMDTreat 6.0 Beta (Office of Surface Mining Reclamation and Enforcement 2022)

frequency of sludge removal from treatment ponds, which decreases the construction and maintenance costs of a treatment system.

The ability to predict long-term chemistry of CMD can be used to inform treatment technology decisions, costs, and goals. For example, Lowber (also known as Marchand) CMD is currently being treated by a passive treatment system, constructed in 2006, that consists of six serially connected oxidation/settling ponds and a wetland for the removal of Fe (Hedin 2008, 2013). In this study, five stages of inferred or measured Lowber CMD chemistry, including the current conditions, were selected as representative cases for the chemical evolution of CMD warranting different treatment strategies (fig. 1). For each period, a treatment strategy was identified for the particular water quality and modelled using AMDTreat 6.0 Beta software and the included PHREEQ-N-AMDTreat tool (Office of Surface Mining Reclamation and Enforcement 2022). The goal of modelling was to demonstrate how treatment liability may change as the water quality evolves from net-acidic to net-alkaline character with progressively lower contaminant concentrations over a decadal timeframe.

## Methods

Five stages of Lowber CMD chemistry (A–E in fig. 1) representing initial first flush (A: 1953–1963), early net-alkaline (B: 1970s), net-alkaline passive treatment installation (C: 2007–2012), current net-alkaline (D: 2020s), and future conditions (E: 2043–2053) were selected from the first-flush model described in the introduction as representative cases. For all cases, the flow was assumed to be constant at 7,098 L/min (1,875 gal/min). A treatment strategy was selected for each representative case using a combination of currently used technologies and those available for simulation by PHREEQ-N-AMDTreat (Cravotta 2021), a geochemical modelling tool capable of simulating changes in pH and solute concentration for various active and passive treatment technologies. Treatment layout and dissolved Fe attenuated were used with AMDTreat 6.0 Beta software to compute capital costs of treatment system construction, annual operations

and maintenance (O&M), including sludge removal, and the net present value for a term of 75 years assuming an inflation rate of 5% and an 8% rate of return in United States dollars (USD). Active treatment systems included a surface aerator with a retention time of 15 minutes to facilitate CO<sub>2</sub> outgassing. Passive treatment systems included a conveyance ditch for initial aeration.

## Results

As the chemistry of Lowber CMD evolves to progressively lower acidity and contaminant concentrations, the treatment strategies can be modified and overall costs decreased (Table 1). Water quality of period A (1953–1963), representing the initial first-flush composition after mine closure, was highly acidic (pH 3.1) with 300 mg/L Fe. At the time, no treatment was in place; however, for simulation of this case, a treatment system was selected to comply with Pennsylvania maximum contaminant levels for permitted mine effluent (Fe 3 mg/L over a 30-day average; 7 mg/L maximum, pH 6–9). We modelled an active treatment system with a surface aerator for decarbonation (retention time 0.25 h), hydrated lime slurry to increase pH to approximately 9, a reaction tank and clarifier (retention time 6 h) with sludge recirculation to precipitate Fe-oxides, and a polishing wetland (retention time 4 h). The resulting treated effluent had a pH of 7.2 and Fe <0.01 mg/L. AMDTreat 6.0 indicated the net present value of this treatment system to be 33.0 million USD for 75 years.

At the beginning of period B, Lowber CMD transitioned to net-alkaline character having pH of 5.8 but with high Fe (173 mg/L). A modelled switch from lime treatment to hydrogen peroxide (35% H<sub>2</sub>O<sub>2</sub> solution) dosing was the only change from period A to B. The H<sub>2</sub>O<sub>2</sub>-treated effluent was estimated to have a pH of 6.0 and <0.01 mg/L Fe. Using H<sub>2</sub>O<sub>2</sub> (annual cost estimate of 417,000 USD) instead of the hydrated lime slurry (annual cost of 868,000 USD), while retaining all other treatment steps, resulted in a treatment system with a net-present value of 19.4 million USD for 75 years. Additionally, a passive treatment system was modelled for period B; however, a retention time of 30 h

was estimated for each of the 6 ponds in order to reach the maximum contaminant limit for Fe which is not realistic; therefore, the active treatment system was considered the only feasible option.

In period C, a passive treatment layout, including the dimensions of six ponds and one wetland and decarbonation in open channel, were modelled in AMDTreat 6.0 to represent the aerobic treatment system installed at Lowber in 2006 (Hedin 2008). The resulting effluent chemistry, determined by PHREEQ-N-AMDTreat, had a pH of 7.8 and Fe of <0.01 mg/L, which is similar to reported effluent chemistry for the passive system (Hedin 2008 2013). The net-present value estimated by AMDTreat 6.0 is 2.35 million USD for capital and O&M requirements. In 2006, the reported capital cost was 1.30 million USD, which is approximately 1.94 million USD in 2023 accounting for inflation. Modelling using AMDTreat 6.0 resulted in an approximate 20% underestimation of the reported capital cost (1.56 million USD), but overestimated O&M costs.

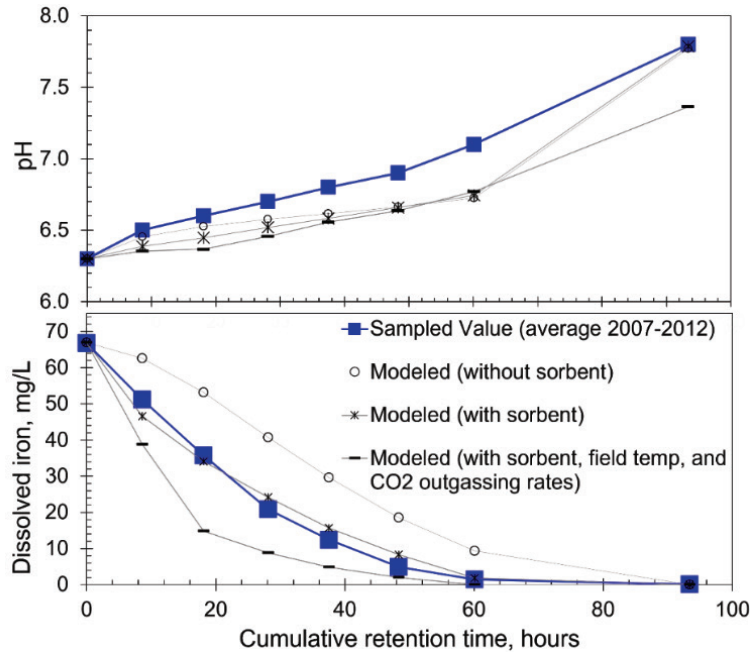
From 2006 to 2020–2021, Fe concentrations decreased from 67 mg/L to 48 mg/L; period D represents the treatment estimates for current CMD conditions using the same treatment layout as period C. Capital costs and

annual O&M costs were similar for periods C and D, but the net-present value decreased approximately 200,000 USD because the annual volume of sludge removal decreased. In period E, the influent pH is similar to periods C and D, but Fe concentrations are projected to be much lower (11 mg/L), so the O&M may be scaled back. The same treatment footprint as periods C and D was modelled, except the depth of the last two ponds were decreased from 1.22 m (4 ft) to 0.61 m (2 ft) and had a retentions time of 5.9 and 5.6 h with the goal of decreasing the annual O&M cost associated with sludge removal. A combination of relatively low Fe in the CMD and scaling back the treatment pond depth resulted in the lowest cost treatment system modelled with a net-present value of 1.72 million USD over 75 years.

The ability to model effluent chemistry with PHREEQ-N-AMDTreat was also considered. Based on the average water-quality of the influent, each pond, and wetland at the Lowber passive treatment system reported by Hedin et al. (2013), key parameters that influence Fe attenuation and pH in the Lowber treatment system were explored. The PHREEQ-N-AMDTreat tool simulates the changes in CMD chemistry as a function of retention time and other

**Table 1** Lowber CMD treatment technologies and cost estimations using AMDTreat 6.0 Beta (Office of Surface Mining Reclamation and Enforcement 2022)

Time Period	Water Quality		Treatment Technology	Capital Cost	Annual	Net Present	Project Footprint
	pH	Fe (mg/L)		USD	O&M Costs	Value	
	Net-acidity (mg/L CaCO <sub>3</sub> )			USD	USD	USD	ha
A:1953-1963	3.1		Active: Decarbonation, Lime, Reaction Tank, Clarifier, Wetland	3,080,000	970,000	33,000,000	0.935
	300						
	1439						
B: 1972-1975	5.8		Active: Decarbonation, H <sub>2</sub> O <sub>2</sub> , Reaction Tank, Clarifier, Wetland	2,580,000	560,000	19,400,000	0.935
	173						
	-23						
C: 2007-2012	6.3		Passive: Decarbonation, Ponds (6), Wetland (1)	1,560,000	42,000	2,350,000	5.19
	67						
	-212						
D: 2017-2021	6.3		Passive: Decarbonation, Ponds (6), Wetland (1)	1,560,000	41,100	2,140,000	5.19
	48						
	-262						
E: 2043-2053	6.38		Passive: Decarbonation, Ponds (6), Wetlands (1)	1,510,000	22,535	1,720,000	5.19
	11						
	-153						



*Figure 2* Lowber CMD pH (upper) and Fe concentrations (lower) during passive treatment. Measured values are sampled averages of the influent, ponds, wetland, and effluent reported by Hedin et al. (2013). PHREEQ-N-AMDTreat model results without sorbent, with sorbent, and with sorbent, recorded field temperatures, and calculated CO<sub>2</sub> outgassing rates

variables for each treatment step. Fig. 2 shows modelled results compared with the average measured pH values and Fe concentration points in blue, connected by a line for ease of comparison. The key parameters explored were the presence of Fe<sup>III</sup>-oxide sorbent, temperature, and outgassing rates of CO<sub>2</sub>. The Lowber system is designed to remove Fe through the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>, followed by Fe<sup>3+</sup> hydrolysis and precipitation to suspended Fe<sup>III</sup>-oxide (Hedin 2008). Sorbent mass, as Fe in mg/L, was estimated as half of the reported total suspended solids (TSS) concentration, assuming TSS is Fe(OH)<sub>3</sub>. This sorbent remains suspended when precipitated and eventually settles as sludge. Lowber CMD without existing sorbent in the system was modelled to represent the CMD in a newly constructed pond, where the only sorbent is fresh precipitate formed from the dissolved Fe of influent. The modelled results assuming only sorption on fresh precipitate underestimated the removal of Fe in all ponds of the system. Conversely, when measured

TSS-estimated sorbent was included in the PHREEQ-N-AMDTreat simulation, the modelled Fe value was consistent with sampled values. This shows the influence of heterogeneous oxidation of Fe<sup>2+</sup> by adsorption onto ferric oxyhydroxide solids that tend to be transported more slowly compared to water and accumulate in a treatment system.

The CO<sub>2</sub> outgassing rate was calculated using the average field temperature, pH, dissolved oxygen and alkalinity values reported by Hedin (2013), which led to overestimation in Fe removal and underestimation in pH values by treatment. P<sub>CO<sub>2</sub></sub> calculations are pH- and temperature-sensitive, and the use of average pH may have affected calculations of CO<sub>2</sub> outgassing rates. By averaging the pH, the resultant reported value may be biased high, resulting in higher estimates of CO<sub>2</sub> as well as larger pH values for “observations” compared to modelled pH values. Regardless, the default CO<sub>2</sub> outgassing rates and temperature were similar to observations, suggesting default

parameters in PHREEQ-N-AMDTreat could be useful without other information.

## Conclusions

This study shows that changes in CMD management strategies may be warranted as CMD chemistry improves on a decadal timescale. AMDTreat 6.0 modelled capital costs, annual O&M, and net-present value were higher for early-stage net-acidic quality that required active treatment technologies. Those costs for alternative treatments decreased through time as net-alkaline conditions with lower contaminant concentrations and passive technologies could be employed. Cost analysis shows that wetlands are more expensive to install than ponds and the installation of a series of ponds give greater potential for resource recovery and maintenance. Default costs of annual O&M were approximately five times greater than the actual O&M costs of the Lowber treatment system; user experience and knowledge of actual costs are essential for making cost estimates of treatment systems. The PHREEQ-N-AMDTreat models indicate key variables affecting CMD treatment include pH and retention time, CO<sub>2</sub> outgassing rate, sorbent availability, and Fe<sup>2+</sup> concentration and oxidation rate. Thus, site-specific information and testing of these parameters may be appropriate when considering treatment design.

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