

Remediation of Coal Mine Drainage with Industrial Byproducts

**The Office of Surface Mining Reclamation and
Enforcement**

Final Project Report

Submitted April 12, 2021

Revised June 2, 2021

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MDTI Cooperative Agreement Number: S18AC20028

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LIST OF ACRONYMS

AL	Action Level
AMD	Acid Mine Drainage
CMD	Coal Mine Drainage
CLT	Column Leach Test
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
EC	Electrical Conductivity
EPA	US Environmental Protection Agency
FA	Fly Ash
ILCD	International Reference Life Cycle Data System
JRC	Joint Research Centre of the European Commission
LCCA	Life Cycle Cost Analysis
LCA	Life Cycle Analysis
L:S	Liquid-to-solid ratio
MCL	Maximum Contaminant Level
MD	Mine Drainage
NRWQC	EPA National Recommended Water Quality Criteria
NWG	Non-woven geotextile
PV	Pore Volume
QAPP	Quality Assurance Project Plan
QF	Quarry Fines
RCA	Recycled Concrete Aggregate
REE	Rare Earth Element
SRB	Sulfate Reducing Bacteria
TRACI	Tool for the Reduction and Assessment of Chemical and other environmental Impacts
WG	Woven Geotextile
WLT	Water Leach Test

1. OVERVIEW

The main goal of this project was to investigate the feasibility of implementing industrial byproducts as sorptive barriers for the neutralization and remediation of coal mine drainages (CMDs) produced from surface coal mining activities. The recycled materials that were tested herein include recycled concrete aggregate (RCA) fines, non-cementitious high carbon fly ash (NC-HCFA), and excess aggregate quarry fines (QFs). These industrial byproducts will be placed between synthetic filters and drain elements, namely geosynthetics, to improve the filtration mechanism and provide uniform flow to the CMD while ensuring long-term retention of the treatment media. *The use of industrial byproducts (that would otherwise have little economic value) offers a sustainable and effective coal mine drainage treatment method.* The results of this research meet the second objective, “Develop innovative solutions to predict MD water-quality problems” outlined by the Mine Drainage Technology Initiative (MDTI) program. Though the impacts of MD treatment on surface water or groundwater were not directly measured in this project, the results from the following objectives allow for better prediction of the potential for mitigating contamination from coal mine drainage through the reuse of materials that would otherwise be considered waste.

1.1 Research Objectives

This research project had the following four main objectives that were completed between 2018-2021:

1) **Determine the effectiveness of RCA fines, excess quarry fines, and off-specification fly ash as media for improving CMD water quality**

Sequential water leach tests (WLTs) of coal mine waste followed by industrial byproducts were conducted to evaluate the remediation potential of these industrial byproducts. The following measurements were made for the effluent solutions collected during WLTs: (1) leaching of metals and metalloids (e.g., Cr, As, Se, Cd), (2) leaching of anions (e.g., nitrate, sulfate), (3) pH, electrical conductivity (EC), and oxidation-reduction potential (Eh), (4) total organic/inorganic carbon, and (5) alkalinity.

2) **Evaluate the impact of CMD treatment on water quality using a flow-through experimental system**

Sequential column leach tests (CLTs) were conducted with three columns to simulate the proposed CMD treatment systems. The first column contained coal mine wastes to generate CMD, the second column contained the industrial byproducts for CMD treatment, and the third column contained soil to test the ultimate impact of this CMD treatment method on ecological health. Woven and unwoven geotextiles were used as filters in columns containing fly ash. Water quality measurements were performed as described in Objective 1.

3) **Simulate water quality under variable field conditions**

Geochemical modeling was performed using the data collected from the sequential WLTs in Objective 1 to determine the dominant oxidation states of the leached contaminants and their leaching control mechanisms.

4) **Evaluate the cost effectiveness of the use of industrial byproducts**

Both the overall costs and the overall benefits, including environmental benefits, of using industrial byproducts in CMD remediation were quantified.

Specifically, the following list of tasks were performed to fulfill the aforementioned research objectives:

Task 1. Literature review: A comprehensive literature review was conducted on the current state of knowledge on CMD and potential solutions including the use of fly ashes, RCA fines, and QFs. The literature review is included in this Final Report as part of the Introduction in section 2 below.

Task 2. Collection of materials: Coal mine wastes were collected from Sub-Bituminous, Bituminous, and anthracite surface mines across the Midwest and elsewhere. Industrial byproducts including off-specification fly ashes, RCA, and QFs were collected from IA and PA. A detailed list of materials collected is provided in section 4 below. Each material was characterized for physicochemical parameters; results from the characterization efforts are shown in Appendix A.

Task 3. Laboratory batch WLTs: These tests were conducted to determine the leaching characteristics of each material in water. Following individual batch WLTs to characterize each material, sequential batch WLTs were conducted in which CMD was generated through batch WLT of each coal mine waste, and then treated by each industrial byproduct. Results from this task are shown in section 4 and Appendix B.

Task 4. Laboratory CLTs: The following sets of CLTs were conducted: (i) preliminary, individual CLTs to test the leaching behaviors of each material, (ii) sequential CLTs of selected coal mine wastes with treatment with selected industrial byproducts and a soil column to test abandoned mine scenarios, and (iii) sequential CLTs of selected synthetic CMDs and selected industrial byproducts to test active mine scenarios. Woven and non-woven geotextiles were used for the fly ash columns. Results from this task are shown in section 5 and Appendix C.

Task 5. Geochemical modeling analyses: These analyses were conducted on selected sequential batch WLT data collected in Task 3 to understand the mechanisms controlling the leaching of metals. Results from this task are shown in section 6 below.

Task 6. Analyses of cost effectiveness and life cycle costs of using industrial byproducts for remediation of CMD: Life cycle analysis and life cycle cost analysis were performed for specific scenarios of CMD treatment with industrial byproducts based on the sequential batch WLT data from Task 3. Results from this task are shown in section 7 below.

Task 7. Dissemination of results: Dissemination efforts are currently underway. The project team expects multiple journal articles based on the project data to be published within 2 years of project completion.

Task 8. Preparation of final report

In this Final Report, we present data generated from this study along with analysis pertaining to the use of select industrial byproducts to treat CMD. All data produced from this study are included in the Appendices

2. INTRODUCTION

Coal plays a vital role in the generation of electricity worldwide. According to the World Coal Association, coal-fueled power plants currently provide 37% of electricity used globally (World Coal Association), and the U.S Energy Information Administration estimates that approximately 30% of the electricity generated in the United States in 2017 was from coal (U.S. Energy Information Administration 2018). The United States is also the second largest coal producer in the world, with over one-fourth of the known coal reserves. However, in spite of its importance in the global energy matrix, coal is a major source of pollution. Not only does burning coal release high amounts of carbon dioxide to the atmosphere, but coal mining disturbs the soil and local ecology, affects water quality, and disrupts hydrological pathways through the discharge of toxic acidic/alkaline water. This polluted water is commonly referred to as coal mine drainage, and it is a major source of both surface and groundwater pollution. For instance, recent surveys have shown that as much as 22% of the rivers in southern West Virginia has been severely affected by alkaline mine drainage (Bernhardt et al. 2012).

Therefore, although coal is a major importance to the global economy, government agencies worldwide are implementing strict rules to mitigate the negative environmental impacts of using coal as an energy source. In terms of coal mining in the U.S, the first set of laws regulating the environmental effects of coal mining was established by the Surface Mining Control and Reclamation Act of 1977 (SMCRA). SMCRA along with its regulations establishes environmental standards that coal mine operators must follow while operating and reclaiming the mined lands. However, only coal mines that ceased operations after August 3, 1977, are regulated under SMCRA. As a result, many of these abandoned mine lands in the United States are a potential source of contamination impacting air, soil, and water. Active coal mines are also a source of contamination as they generate large amounts of polluted water during operations. Examples of coal mine drainage from across the world are illustrated in Figure 1 (Kefeni et al. 2017).

Coal mine drainage (CMD) can be acidic or alkaline and often comprise high levels of iron (Fe), aluminum (Al), and sulfate (SO_4^{2-}) as well as traces of lead (Pb), nickel (Ni), copper (Cu), manganese (Mn), cadmium (Cd), and zinc (Zn). The pH of mining streams mainly depends on the geology of the mined area. For instance, water drainage from Mauriliden mine in Sweden is highly acidic (pH 2.3) with high amounts of Zn and Fe compared to other metals (Hedrich & Johnson 2014), while drainage from Tharsis mines in Spain show predominance of Al, Mg and sulfates (SO_4^{2-}) and pH values as low as 1.8 at some locations (Valente et al. 2013). In general, CMD is acidic and is often called acid mine drainage (AMD). Acid mine drainage is generated during mining activity when sulfide mineral ores such as pyrite are exposed to the atmosphere, and subsequently oxidized to sulfate (SO_4^{2-}) ions by oxygen, water and microorganisms. The resulting sulfate ions are converted into sulfuric acid, which corrodes the surrounding rocks and releases metal ions into solution (Jones & Cetin 2017). Alkaline drainage typically results from weathering of rocks containing carbonates, which act as a buffer for the sulfuric acid produced (Bier et al. 2015). Alkaline mine drainage is characterized by high concentrations of trace metals and salinity as well as more basic pH values than seen in AMD.



Figure 1. (A) AMD effluents, (B) blooms of secondary efflorescent minerals in Morocco (Khalil et al. 2014). (C, D) CMD in South Africa (Clay et al. 2013). (E) Acid mine drainage residuals in Pennsylvania (US Geological Survey). (F) Stream impacted by acid mine drainage in the Mid-Atlantic USA (US Environmental Protection Agency).

The alkaline or acidic nature of the coal mine drainage combined with the high metal concentrations are extremely detrimental to the environment, representing a major threat to aquatic life, soil ecology and water quality of surrounding ecosystems. Furthermore, oxidation of sulfide bearing rocks generates metal oxide precipitates, which can deposit onto soil and ocean beds and become bioavailable to organisms at the bottom of the food chain at greater concentrations. Therefore, these metal contaminants can potentially be transported and accumulated across different trophic levels due to predator-prey interactions. For instance, to assess the negative effects of acid mine drainage on fish, Talukdar et al (2017) performed a laboratory experiment where *Channa punctate* fish were exposed to waters contaminated with 10% AMD for 30 days. Results of this study showed that AMD caused significant morphological, histological and hematological changes as well as disruption of DNA in the AMD exposed fish compared to the control group. Furthermore, Bier et al. (2014) investigated the differences in the microbial communities over a gradient of alkaline mine drainage in Central Appalachian streams. Their study found a negative correlation between microbial diversity and the concentrations of Cd, Mn, Zn and Ni while no correlation was found between the microbial diversity and pH gradients nor the extent of upstream mining. This type of study is particularly important because information on the relationship of microbial communities with coal mine drainage can be used to develop bio-

indicators. Thus, it can be used to assess the quality of the environment and how it changes over time (Holt & Miller 2010).

Treatment of CMD can be very challenging due to the large variety of contaminants and their corresponding concentrations. Most of the CMD remediation has been done by pH neutralization and stabilization of toxic contaminants (typically through precipitation). This technique usually includes the addition of alkaline chemicals such as calcium hydroxide ($\text{Ca}(\text{OH})_2$), limestone (CaCO_3) and caustic soda (NaOH) to chemically precipitate metals as metal hydroxides/carbonates and sulfate as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). However, this technique involves the generation of large amounts of sludge, which is discarded in landfills, and continuous addition of virgin materials for pH neutralization, thus making the process expensive and unsustainable. Moreover, the effectiveness of this technique depends on the neutralizing capacity of the agent that is utilized. For instance, NaOH is 1.5 times more effective than $\text{Ca}(\text{OH})_2$, but it costs nine times more (Johnson & Hallberg 2005). Other commonly utilized treatments include; ion exchange, adsorption, permeable reactive barriers, membrane filtration and biological treatment using wetlands and sulfate-reducing bioreactors (Fu & Wang 2011). Table 1 summarizes the most relevant treatment alternatives for acid mine drainage, and highlights the advantages and disadvantages of each option. In most cases, aeration and addition of alkaline agents are used to treat active mines, whereas for abandoned/decommissioned mines the use of wetlands is most common (Cravotta III & Brady 2015).

Currently researchers are studying more sustainable and cost effective solutions such as microbial driven processes and the utilization of industrial byproducts, which can decrease the treatment costs while reducing the waste loading to landfills. Most commonly tested byproducts include cement kiln dust, lime kiln dust, red mud bauxite, coal fly ash, and blast furnace slag (Kefeni et al. 2017). Several studies have investigated the utilization of fly ashes with mine tailings to reduce the effluent pH and decrease metal concentrations from acid mine drainage. Shang et al. (2006) treated acidic drainage from Sudbury Mine, Canada and decreased the trace element concentrations in the effluent to below the local regulatory standards. Mohamed et al. (2007) showed that a mixture of Al, lime and fly ash was effective in reducing the leachability of heavy metals from the mine tailings collected from Quebec, Canada. Furthermore, Jones & Cetin (2017) conducted column leaching tests to evaluate the use of different fly ashes and recycle concrete aggregates (RCA) for remediation of AMD. They found that RCAs and one of the highly alkaline fly ashes tested were the most effective materials for raising the pH of AMD and reducing the metal concentrations below the Environmental Protection Agency Drinking Water Quality Standards. This study also showed that sulfate concentrations of AMD decreased considerably when it was treated with RCAs. However, such trend was not observed for the fly ashes used in that study. Madzivire et al. (2014) showed that fly ash treated AMD had lower amounts of toxic elements, radioactive compounds and sulfate ions, and this treatment yielded high quality water suitable for irrigation applications.

Nevertheless, the best way to minimize environmental impacts from mining activities is the implementation of preventative measures, which includes protecting sulfide ores from oxidizing agents (i.e., oxygen, water and microorganisms) (Kefeni et al. 2017). The most common techniques are flooding/sealing underground mines, underwater storage of tailings, land-based storage in sealed waste heaps, blending of mineral wastes, total solidification of tailings, addition of anionic surfactants, and coating (Johnson & Hallberg 2005). However, these treatment methods have limitations; for example, flooding/sealing is only effective if there is no infiltration of oxygen-

containing water, and consequently remediation processes must be implemented to minimize environmental impacts.

In an effort to make CMD remediation more economically viable, researchers and industries are investigating ways to recover some of the contaminants. According to Stewart et al. (2017), the iron-rich precipitates from CMD can be utilized in pigments, agricultural phosphorous control and heavy metal remediation. In particular, this study analyzed 18 different CMD effluents as well as 22 treated precipitates from the Appalachian Basin to look for rare earth elements (REE) and yttrium, which are mainly used to produce electronics. They found that possessed the amount of REE and yttrium in CMD streams were 1-4 orders of magnitude higher than those observed in natural waters. Moreover, the results of this study showed that concentrations of these elements in CMD streams are inversely proportional to the discharging pH. Kefeni et al. (2017) highlighted that the most valuable resources obtained at the lab scale are ferric hydroxide, ferrite, barium sulphate, gypsum, rare earth elements, sulfur and sulfuric acid. Furthermore, recovery of sulfuric acid, metals such as Cu, Zn, Co and Ni as well as Fe-oxides have also been studied. Marketing of these recovered chemicals and recycling mining materials could help to offset the treatment costs for CMD, and make the whole process more sustainable. Furthermore, several studies have investigated the use of mine waste such as coal gangue and mine tailings to fill underground mines which could also provide a sustainable and economic solution (Wu et al. 2017; Park et al. 2014).

In order to minimize the harmful effects of mining activities to the environment, an evaluation of all pollution sources along the production chain is necessary. Currently, this evaluation is mainly achieved through a life cycle assessment (LCA), which takes direct and indirect mining impacts into account. Examples of direct effects include processing mining waste, methane generation, and drainage water, whereas indirect impacts accounts for energy consumption and the production of raw materials. For instance, Burchart-Korol et al. (2016) built a computational LCA model including direct and indirect effects based on the data of 31 mines located in Portland, Oregon. The system boundary diagram used in this study is shown in Figure 2. Results of this study showed that CMD water, processing waste and methane emissions had the highest environmental impacts followed by electricity consumption, heat and steel support. On the other hand, Khalil et al. (2014) used GIS and remote sensing tools & techniques to assess the influence of an abandoned mine in Morocco to its surrounding environment. This research provided an environmental database that could be used to develop remediation measures to the affected area.

In conclusion, the importance of coal in the energy matrix and the plethora of harmful environmental effects associated with coal mining makes it difficult for environmental agencies worldwide to implement policies and regulations to protect the environment while keeping the coal exploration profitable. In this scenario, there is an increasing need for solutions that are effective in reducing CMD pollution, and at the same time sustainable and cost effective. As mentioned in this review, many researchers have been looking into new treatment processes such as those evaluating microbial driven treatment processes and the use of waste materials to neutralize pH and precipitate metals. Others are investigating the recovery of valuable materials from contaminated leachate and working on predicting the overall impact of mining operations to the environment. All approaches discussed here are complementary and can be used for mining operations at a global scale.

Table 1. Summary of treatment alternatives for AMD with their respective advantages and disadvantages (reproduced from Kefeni et al. (2017)).

Treatment Options	Advantages	Disadvantages
Passive: Carbonate, lime, marble, fly ash	Cost-effective relative to active treat	Overdose may mobilise contaminants
Bentonite clay composite	Effective at small scale	Requires shaking
Biochar	Reduce acidity and metal toxicity	Insignificant, difficulty of resource recovery
Bone meal	Cost effective; Effective passive treatment of AMD	Need to be heated at 500°C, cleaned, crushed,boiled and dried; difficult to achieve higher pH
BOS Sludge	Cost effective relative to alkaline industrial chemicals	Insignificant
Cellulosic waste + SRB ¹	Cost-effective, relative to alkaline chemicals	Slow rate of metal removal
Chicken manure + SRB	Effective than dairy manure and sawdust	Add high organic loads
Coal fly ash	Efficient and cost-effective relative to lime or limestone	Not suitable for recovery of metals from the waste due to elevated concentration of a radioactive element
Crushed seashell	Cost-effective	Not available as required; needs to be crushed
Dairy manure compost	Generate minimum toxic sludge, cost effective relative to alkaline chemicals	Requires pH adjustment for selective metal removal
Dead Bacillus drentensis sp. In polysulfone polymer	No continuous nutrient supply required,effective at lower pH for toxic metal removal from AMD affected groundwater	Insignificant
Dunite	Cost effective, removes most of the metals from AMD	Need to be crushed and sieved
Electrochemical neutralisation	“No chemicals added to remove chemicals” Forms sulphuric acid	Cathode corrosion may occur in the presence of excess Fe(III) in AMD
Electrodialytic	More effective than the conventional lime treatment	Expensive, fouling
Fe ₃ O ₄ nanoparticles	Fast and effective for metal removal, reuse of nanoparticles	insignificant
Filamentous green algae	Cost-effective relative to alkaline industrial chemicals; could be reused	pH dependent adsorption
Food based waste compost and Zeolite	Effective for prevention of AMD generation from tailing	insignificant
Lignite	Nontoxic and cost-effective compared to alkaline industrial chemicals	Used for selective metal removal, over dosage may add additional contaminants
Lime nanoparticles	Fast and effective than conventional lime treatment	Expensive
Manure + SRB	Efficient and cost-effective, compared to active treatment	Insignificant
Marble stone powder (calcite tailing) + SRB	Effective for passive neutralisation of AMD	The treated AMD water, could be used only for irrigation
Membrane	Almost complete contaminant removal	Expensive, membrane fouling, brine generation
Pig slurry and marble waste	Effective for metal removal (Cd, Pb, and Zn)	Poor Cu removal
Spent mushroom substrate	Effective for passive treatment of coal mine drainage	Used only for pH greater than 3, and not effective for the removal of Mn and dissolved ferric
SRB	Metals removed as sulphide precipitate	Takes longer time for complete removal of contaminants
Steel slag leaches beds	Improved alkalinity	Decrease of alkalinity over time
Wood ash mixed with sand	Effective for removal of high concentration of Fe(II) from sulphate reducing passive bioreactors effluent	Requires more than 3 months for almost complete removal of Fe(II) as Fe(OH) ₃ precipitate
Zeolite	Good metal binding capacity and readily available	Low removal efficiency
Zero-valent iron nanoparticles	Effective for both organic and inorganic removal	No significant disadvantage

¹SRB: sulfate reducing bacteria

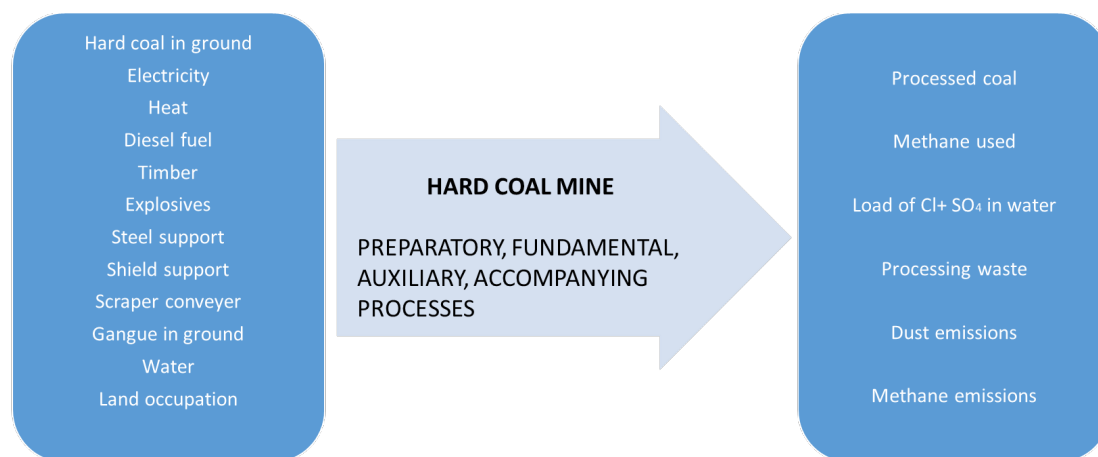


Figure 2. LCA modelling system diagram adapted from (Burchart-korol et al. 2016).

Through this literature review, we found that previous studies such as Jones & Cetin (2017) have showed that RCAs and fly ashes were effective in the treatment of acidic mine drainages which had similar characteristics to CMD. However, the effect of these treatment methods on the microbial ecology of surrounding environment as well as the cost effectiveness compared to traditional remediation methods was not evaluated. In addition, few studies evaluated the use of waste byproducts alone to treat CMD, or have applied their proposed treatment to CMD from different sources. In contrast, the current project will investigate the use of quarry fines, off-specification fly ashes as well as RCAs to treat the CMD leached from Bituminous, subBituminous, and anthracite coal refuses. In addition, this research project will investigate the influence of each treatment on the microbial ecology of the surrounding environment and the water quality of the treated effluent. A cost comparisons of each proposed treatment to traditional remediation techniques will also be conducted. Therefore, the robustness of our study in terms of the amount and diversity of industrial byproducts tested, and parameters analyzed has the potential to significantly enhance and advance the knowledge of sustainable CMD treatment technologies.

3. QUALITY ASSURANCE

A data quality assurance project plan (QAPP) for effective quality control was carried out throughout the project activities. In this QAPP, the following data quality objectives were met: (i) the quality of all input and calibration data will be known and documented, (ii) the data will provide sufficient coverage of relevant parameter ranges, and (iii) the data will be comparable with respect to previous studies where available. Specifically, for all laboratory-generated data, the following specific acceptance criteria for measurements were implemented:

1. Accuracy of $\pm 10\%$ or 0.1 pH units. Accuracy describes how close the measurement is to its true value, which was routinely tested in each measurement run on all equipment by analyzing laboratory-prepared calibration standards or matrix spike samples.
2. Precision of $\pm 20\%$. Precision was tested routinely by analyzing select replicate samples. A less stringent criterion was adopted herein due to the inherent heterogeneity of coal mine drainage samples. Repeat measurements of the same samples were used to determine the

precision in cases where the heterogeneity between replicate reactors/samples were too large.

3. Completeness of at least 95% sampled were analyzed for each water quality parameter.

Tests were repeated when samples did not comply to the above acceptance criteria. The data reported herein have passed the quality control criteria.

4. OBJECTIVE 1: Determine the effectiveness of industrial byproducts as media for improving CMD water quality

Coal refuse, off-specification fly ash, quarry fines, and recycled concrete aggregates (RCA) were collected from around the Midwest as well as from Pennsylvania (Table 2). Specifically, coal refuses collected for this project included Bituminous, Sub-Bituminous, and anthracite coals. Off-specification fly ashes were collected from power plants that used Sub-Bituminous and anthracite coals, collected quarry fines predominantly consisted of limestone (CaCO_3) and dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$), and RCAs were collected from wastes from demolished buildings and pavements. The fly ash used in this study had high carbon content and therefore, were considered to be off-specification. In general, all leach tests in this objective were conducted following the EPA Leaching Environmental Assessment Framework (LEAF) guidance.

Table 2. List of collected materials.

Materials	Type	Materials ID	Location
Coal Refuse	Sub-Bituminous Coal	Sub-Bituminous-BM	Blom Mahaska, IA
	Sub-Bituminous (Abandoned)	Sub-Bituminous-NQ	Newquist, IA
	Sub-Bituminous (Muscatine Power Water)	Sub-Bituminous-MP	Gillette, WY
	Bituminous - Coarse	Bituminous -Coarse	Sunrise Coal Mine, IN
	Bituminous - Fine	Bituminous -Fine	Sunrise Coal Mine, IN
	Anthracite	Anthracite-Eckley	Eckley Mine, PA
	Anthracite	Anthracite-Harry	Harry East Mine, PA
Off-Specification Fly Ash	Sub-Bituminous (Fresh)	Sub-Bituminous FA-FR	Muscatine Power & Water, Muscatine IA
	Sub-Bituminous (Stockpiled)	Sub-Bituminous FA-SP	Muscatine Power & Water, Muscatine IA
	Sub-Bituminous- Alliant Energy (stockpiled)	Sub-Bituminous FA-AE	Prairie Creek-Cedar Rapids, IA
	Anthracite	Anthracite FA-NH	Northampton, PA
Quarry Fines	Limestone	Limestone QF	Ames, IA
	Dolomite	Dolomite QF	Clinton, IA
Recycled Concrete Aggregates (RCA)	Demolished waste	RCA-B	Ankeny, IA
	Pavement waste	RCA-P	Ames, IA

4.1 Materials characterization

Prior to conducting batch WLTs, each type of material was characterized for electrical conductivity (EC), oxidation-reduction potential (Eh), buffering capacity, specific gravity (G_s), X-ray diffraction patterns, thermogravimetric trends, and metals content. Select data are shown in Table 3; the remaining data are provided in Appendix A. The associated experimental methods are also described in the Appendix A.

Of particular interest was the pH and buffering capacities of each material. We note that as expected, most of the coal refuses produced leachate that had acidic pH except for the Bituminous coal from Sunrise Coal Mine, IN and the Sub-Bituminous coal from WY. Most of the industrial byproducts (off-specification fly ashes, quarry fines, and RCAs) had basic pH, making them appropriate treatment media for neutralizing the acidity of CMD. In addition, the buffering capacities were higher in most industrial byproducts compared to coal refuses, pointing to the likelihood that these materials would indeed be adequate for neutralization.

Table 3. Values of pH, Eh (redox potential), EC (electrical conductivity), G_s (specific gravity), and buffering capacity for all collected materials.

Materials	Type	Location	pH	EC (mS/c)	Eh (mV)	G_s	Buffering capacity (meq acid)
Coal Refuse	Anthracite	Harry East Mine, PA	4.7	80	250	2.08	1
	Anthracite	Eckley Mine, PA	3.96	124	515	2.21	1
	Bituminous Coarse	Sunrise Coal Mine, IN	8.36	984	452	2.19	3.4
	Bituminous Fine	Sunrise Coal Mine, IN	6.85	4.4	469	2.36	1.3
	Sub-Bituminous Coal	Blom Mahaska, IA	3.4	5	516	2.46	1.2
	Sub-Bituminous (Abandoned)	Newquist, IA	3.5	9	524	2.48	1.2
	Sub-Bituminous (Muscatine Power & Water)	Gillette, WY	8.9	346	241	1.47	2.5
Off-Specification Fly Ash	Sub-Bituminous	Prairie Creek-Cedar Rapids, IA	12.4	8	-31	1.70	19
	Sub-Bituminous (Fresh)	Muscatine Power & Water, Muscatine IA	12.3	5	-102	1.46	18.2
	Sub-Bituminous (Stockpiled)	Muscatine Power & Water, Muscatine IA	12.6	14.5	-102	1.39	19.5
	Anthracite	Northampton, PA	10.1	2	204	2.69	4
Quarry Fines	Limestone	Ames, IA	9.4	441	206	3.06	20
	Dolomite	Clinton, IA	8.36	1.7	194	2.37	9
RCA	Demolished waste	Ankeny, IA	12.0	2.6	-165	2.62	14.5
	Pavement waste	Ames, IA	11.9	1.7	24	2.64	6.6

4.2 Batch water leach test (WLT) design

Following materials characterization, we performed single and sequential batch WLTs to determine the leaching behaviors of most materials listed in Table 2 with special attention to pH, EC, Eh, alkalinity, total organic and inorganic carbon, sulfate, nitrate, and metals concentrations. Anthracite coal refuses were excluded from these WLTs and subsequent experiments due to the low occurrence of anthracite-burning power plants. The batch WLTs were conducted following EPA method 1313 or 1316. The water quality analyses were conducted following standardized methods as shown in Table 4. It is important to note that the metals listed in Table 4 were chosen for quantitative measurements following preliminary qualitative analysis. Other metals such as Hg, Pt, and Tl were not detected and hence, were not included in the quantitative analysis.

Each CMD and industrial byproduct leachate exhibited unique water quality characteristics in the single batch WLTs conducted following EPA method 1313. Those results are provided in Appendix B. However, in this final report, we focused on the sequential batch WLTs as this set of experiments effectively tested the “worst-case scenarios” of pollution in each CMD and the outcome of each CMD treatment. Sequential batch WLTs were conducted following EPA method 1316. In brief, all materials were air dried for 24 hours and crushed using a hammer to pass number 50 sieve (<0.297 mm) prior to leachate extractions. Briefly, a liquid-to-solid ratio (L:S) of 10:1 was used, in which 200 ml of ultrapure water (leachant) was added to extraction vessels containing 20 g of dried coal waste materials. The extraction vessels were rotated at 29 revolutions per minute for 24 hours at ambient temperature.

Following the extraction, the coal waste mixtures were filtered through 1.5 µm pore size filters and the leachate was considered a CMD effluent. This filtered leachate was used as influent for a second batch extraction test, which was performed using the industrial byproducts to simulate CMD treatment (see Figure 2). Water quality analyses outlined in Table 4 were performed in the leachate of both batch extractions to determine the effectiveness of CMD treatment by each industrial byproduct used.

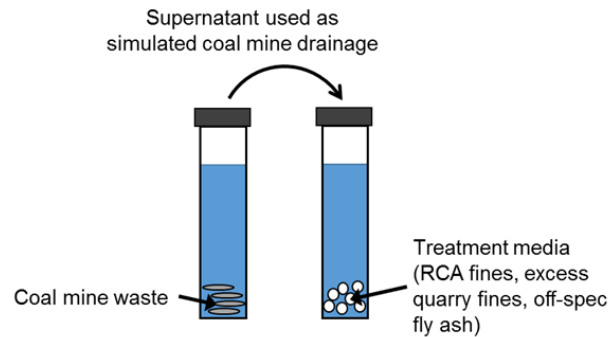


Figure 2. Diagram for the sequential batch leaching tests

Table 4. Summary of water quality analyses performed.

Analyses	Parameters	Methods
Water chemistry analyses	Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC)	Standard methods 5310 C
	Oxidation-reduction potential (Eh), conductivity (EC), and pH	U.S. EPA 9045D
	Alkalinity	EPA-102-A Rev. 3
	Sulfate	EPA-123-A Rev.5
	Nitrate and Nitrite	EPA-115-A Rev.6 EPA- 114-A Rev. 10
Metal analyses	Al, Ag, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Si, Sr, V, and Zn	U.S. EPA 6010B

4.3 Single batch WLT results for coal refuses

Though each material was tested in single batch WLTs, we focus herein on tests with coal refuses in which the leachates are equivalent to CMD. As shown in Table 5, most coal refuses except for fine coal refuse from Sunrise coal mine generated acidic CMD. Other than pH, the most notable water quality parameter of concern in the generated CMD samples was sulfate for which the concentrations ranged from approximately 60 mg/L to over 1,200 mg/L (secondary maximum contaminant level (MCL) = 250 mg/L). As such, results for pH and sulfate measurements will be shown for sequential WLTs and CLTs.

Table 5. Water quality results of CMD generated from each coal refuse material.

Source	pH	Redox (mV)	Alkalinity (mg CaCO ₃ /L)	Nitrate (mg N/L)	Sulfate (mg/L)	DOC (mg C/L)	DIC (mg C/L)
Blom Mahaska	4.07	479.50	142.91	0.36	595.36	3.63	0.52
Newquist	3.76	426.00	66.85	0.17	1270.08	7.74	0.49
Muscatine Power & Water	6.51	314.00	47.35	0.25	58.63	16.26	2.67
Sunrise coal mine (coarse)	3.47	295.00	-6.01	0.39	1201.34	3.10	0.40
Sunrise coal mine (fine)	4.78	125.77	12.80	0.41	726.36	2.63	0.66

Of the metals quantitatively measured, As, Be, Cd, Cr, Cu, Li, Mo, Ni, Pb, Se, and V were detected (at levels near or exceeding EPA regulatory limits) in the generated CMD samples from single batch WLTs of coal refuses or in sequential WLTs discussed below. In particular, in the CMD samples, significantly high levels of As, Cd, Mo, Ni, Pb, and Se were observed (Figure 3). Most of the other metals shown in Figure 3 (Be, Cr, Cu, Li, and V) were present in relatively high concentrations following at least some of the treatments with industrial byproducts in the sequential batch WLTs (see section 4.4). The known regulatory limits set by the US Environmental Protection Agency or state agencies are provided in Table 6.

Table 6. Regulatory limits of select metal analytes.

Metal	Type of regulatory limit	Limit (mg/L)
As	US EPA maximum contaminant level (MCL)	0.01
Be	US EPA MCL	0.004
Cd	US EPA MCL	0.005
Cr	US EPA MCL	0.1
Cu	US EPA action level	1.3
Li	N/A	N/A
Mo	US EPA National Recommended Water Quality Criteria (NRWQC) (human health) limit	0.05
Ni	US EPA NRWQC (human health) limit	0.61
Pb	US EPA action level	0.015
Se	US EPA MCL	0.05
V	CA State Water Resources Control Board drinking water notification levels	0.05

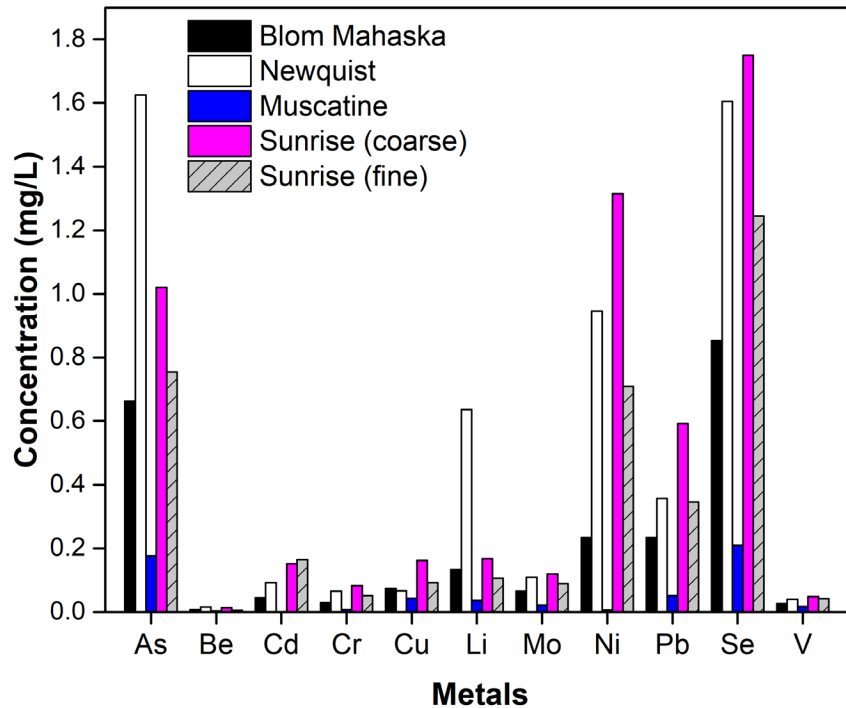


Figure 3. Select metal concentrations detected in CMD generated through single batch WLTs of coal refuses.

4.4 Sequential batch WLT results

4.4.1 Blom Mahaska CMD treatments by industrial byproducts

As shown in Table 5, Blom Mahaska CMD had an acidic pH of approximately 4.1, which was increased following treatment with all industrial byproducts (Figure 4). In fact, the majority of industrial byproduct treatments resulted in a final leachate pH above 10 with a few treatments resulting in corrosive alkaline pH (all Sub-Bituminous fly ashes and RCA from demolished waste). Sulfate concentrations increased following all industrial byproduct treatments except for anthracite fly ash and RCA from demolished wastes (Figure 5). Sulfate concentrations in the final leachates in all treatments exceeded the MCL of 250 mg/L by over 150 mg/L.

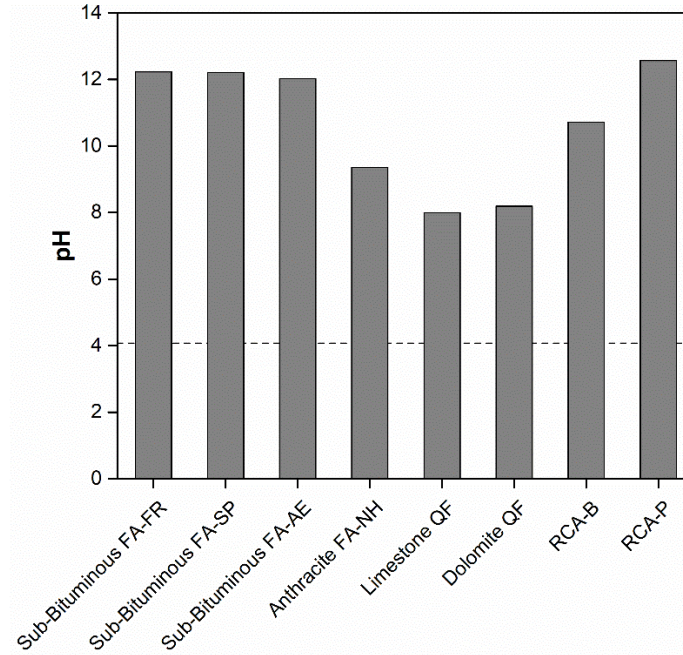


Figure 4. pH of Blom Mahaska CMD following treatment with each industrial byproduct. The dashed line indicates the initial pH of the CMD.

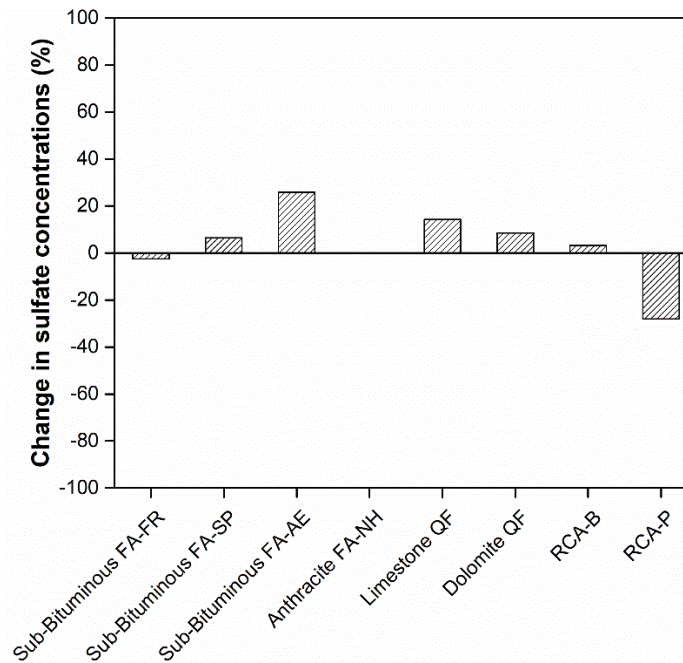


Figure 5. Percent changes in sulfate concentrations of Blom Mahaska CMD following treatment with each industrial byproduct.

While most metals concentrations decreased following most industrial byproduct treatments, some metals were present in higher concentrations compared to the CMD after treatment (Figure 6). Specifically, treatment with all fly ashes appeared to result in increased concentrations of Li, Mo,

and V compared to the CMD, suggesting that fly ashes were not only ineffective in removing these metals from the CMD, but also that these materials serve as the source of additional pollution of select metals. At the same time, however, the fly ashes were most effective in removing other metals such as As, Cd, and Cu. Overall, limestone quarry was able to remove most metals shown even though the percentages of removal were relatively low.

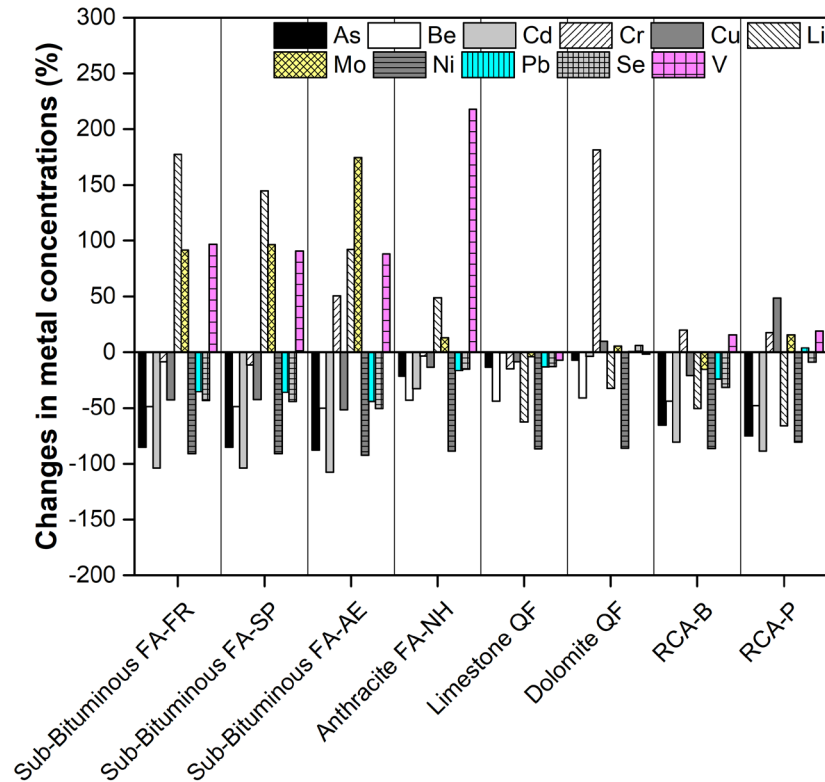


Figure 6. Percent changes in metals concentrations of Blom Mahaska CMD following treatment with each industrial byproduct.

4.4.2 Newquist CMD treatments

As shown in Table 5, Newquist CMD had an acidic pH of approximately 3.8, which was increased following treatment with all industrial byproducts (Figure 7). Similar to Blom Mahaska CMD treatment discussed in section 3.4.1, many of the industrial product treatments resulted in highly basic pH including all Sub-Bituminous fly ashes and RCA from demolished waste. Unlike Blom Mahaska CMD, Newquist CMD treatment with RCA from pavement waste only raised the pH to approximately 8.5 (instead of >10 as seen for Blom Mahaska CMD).

Decreases in sulfate concentrations were observed following treatment with most industrial byproducts except for dolomite quarry fines (Figure 8). It is interesting to note that although Blom Mahaska CMD and Newquist CMD had similar sulfate concentrations of approximately 1,200 mg/L, the treatment effectiveness for sulfate removal by industrial byproducts were considerably different. For example, treatments using anthracite fly ash, limestone and dolomite quarry fines, and RCA pavement waste were all 15-50% less effective in removing sulfate from Newquist CMD

compared to Blom Mahaska CMD. Sulfate concentrations in the final leachates in all treatments exceeded the secondary MCL of 250 mg/L.

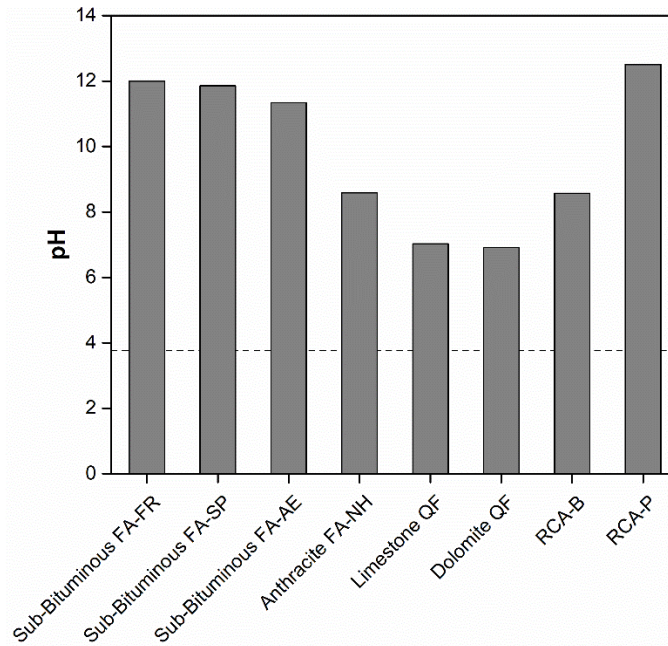


Figure 7. pH of Newquist CMD following treatment with each industrial byproduct. The dashed line indicates the initial pH of the CMD.

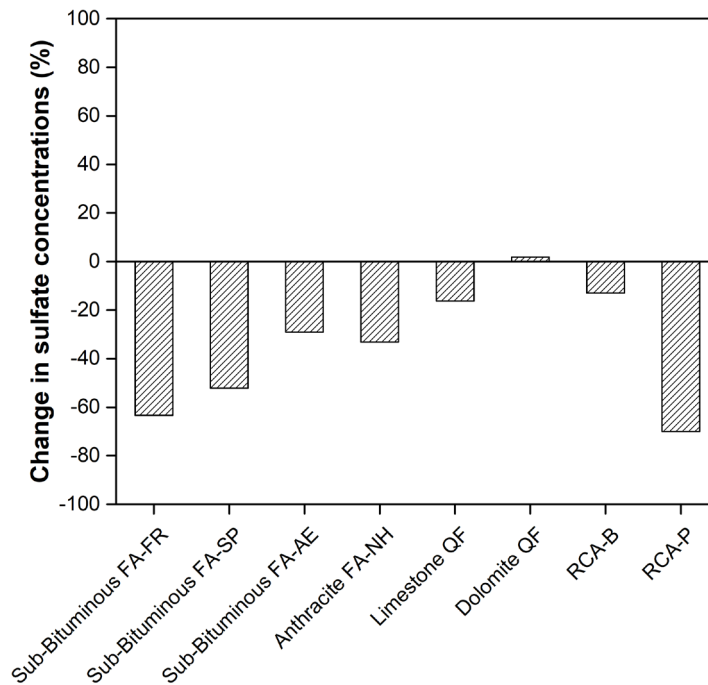


Figure 8. Percent changes in sulfate concentrations of Newquist CMD following treatment with each industrial byproduct.

Metals removal by industrial byproduct treatment of Newquist CMD had overall similar trends as observed for Blom Mahaska CMD (Figure 9). All fly ashes appeared to add to, instead of removing, Mo and V pollution. No industrial byproduct treatment was able to remove all metals discussed here; however, dolomite quarry fines and pavement RCA appeared to contribute to better removal of most metals compared to the other treatments overall.

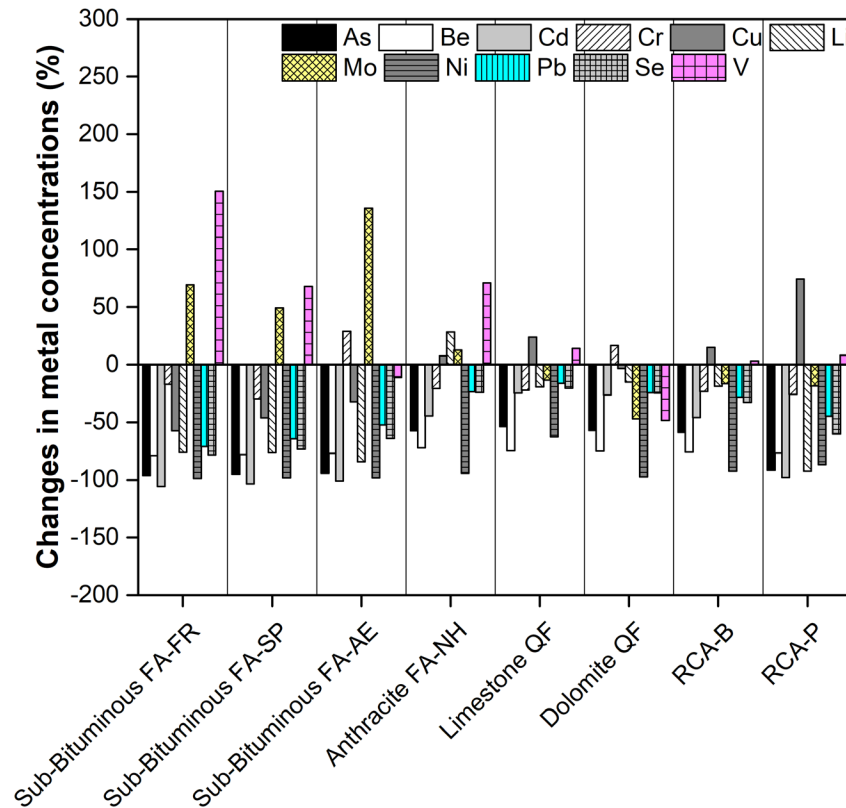


Figure 9. Percent changes in metals concentrations of Newquist CMD following treatment with each industrial byproduct.

4.4.3 Muscatine CMD treatments

As shown in Table 5, Muscatine CMD had a near-neutral pH of 6.5, which was increased following treatment with all industrial byproducts (Figure 10). Overall, changes in pH due to treatments were similar to what was observed for Blom Mahaska CMD treatment discussed in section 3.4.1.

All industrial byproduct treatments of Sunrise fine CMD were ineffective in removing sulfate (Figure 11); instead, all treatment materials added to the existing sulfate pollution from the CMD. That being said, the CMD itself had very low sulfate concentrations (~60 mg/L), indicating that all industrial byproduct treatments resulted in additional sulfate leaching from the materials themselves.

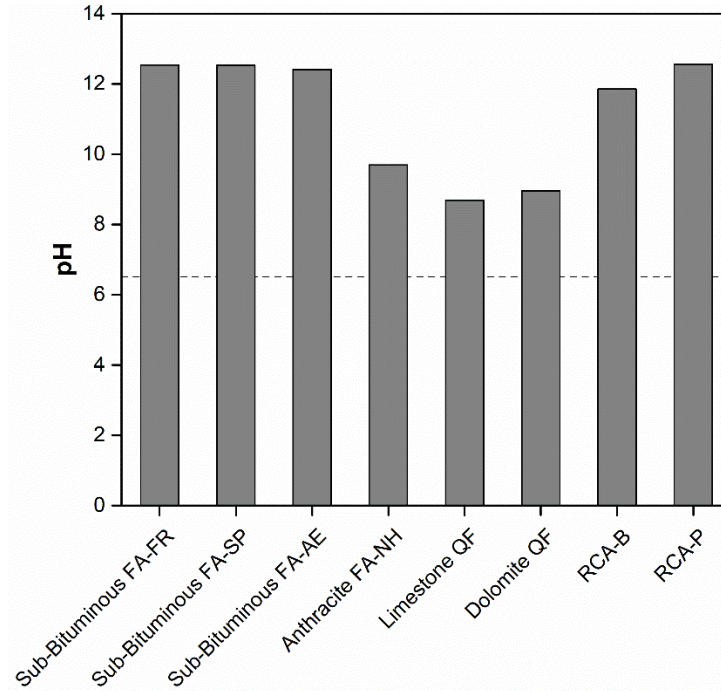


Figure 10. pH of Muscatine CMD following treatment with each industrial byproduct. The dashed line indicates the initial pH of the CMD.

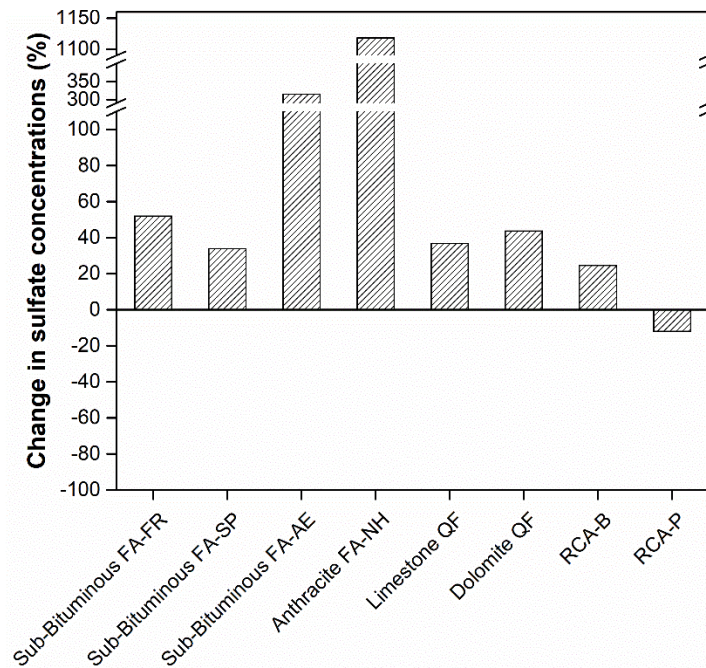


Figure 11. Percent changes in sulfate concentrations of Muscatine CMD following treatment with each industrial byproduct.

Metals removal by industrial byproduct treatment of Muscatine CMD was largely ineffective with most treatments resulting in considerable additional inputs of metal pollution (Figure 12). In particular, treatment with all fly ashes resulted in over 500% increases in Li and Mo concentrations in the final leachate along with over 200% increases in Cr and V concentrations. Limestone quarry fines treatment resulted in the least overall increases in metals compared to other treatments. It is noteworthy that Muscatine CMD had lower concentrations of most metals compared to other CMDs, which is likely the reason behind these large increases in metals concentrations following industrial byproduct treatments.

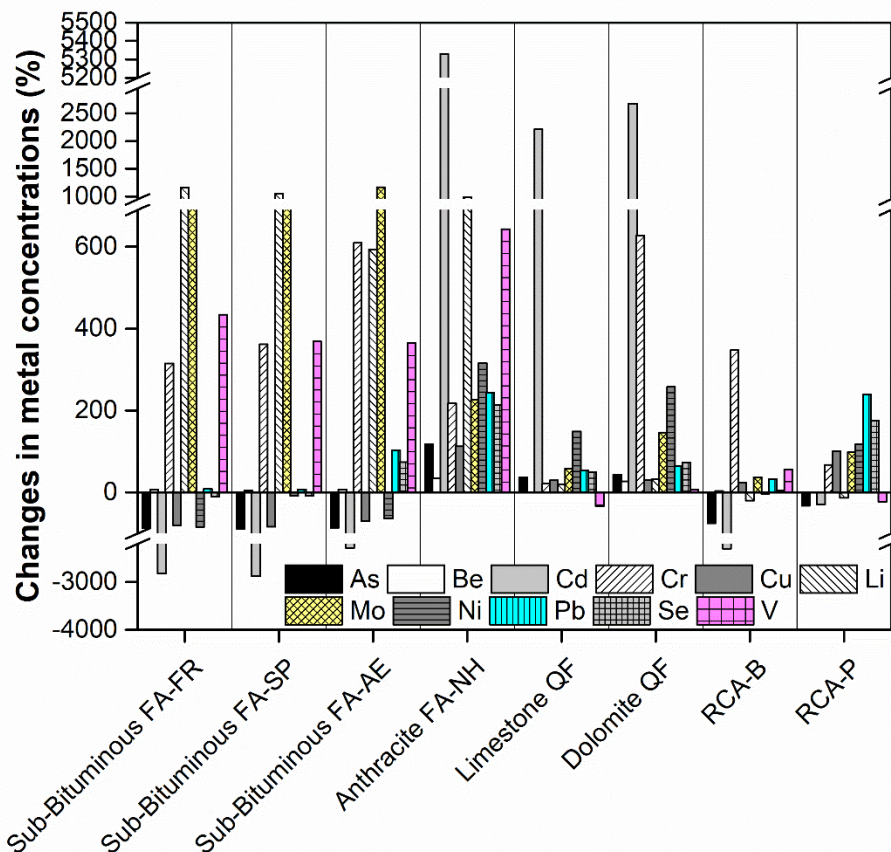


Figure 12. Percent changes in metals concentrations of Muscatine CMD following treatment with each industrial byproduct.

4.4.5 Sunrise coarse CMD treatments

As shown in Table 5, Sunrise coarse CMD had an acidic pH of approximately 4.8, which was increased following treatment with all industrial byproducts (Figure 13). Overall, changes in pH due to treatments were similar to what was observed for Blom Mahaska CMD treatment discussed in section 3.4.1.

Most industrial byproduct treatments of Sunrise coarse CMD were effective in removing over 30% of sulfate from the CMD (Figure 14). None of the final leachates had sulfate concentrations lower

than the MCL, likely due to the high starting sulfate concentration (1,200 mg/L as shown in Table 5) in the CMD itself.

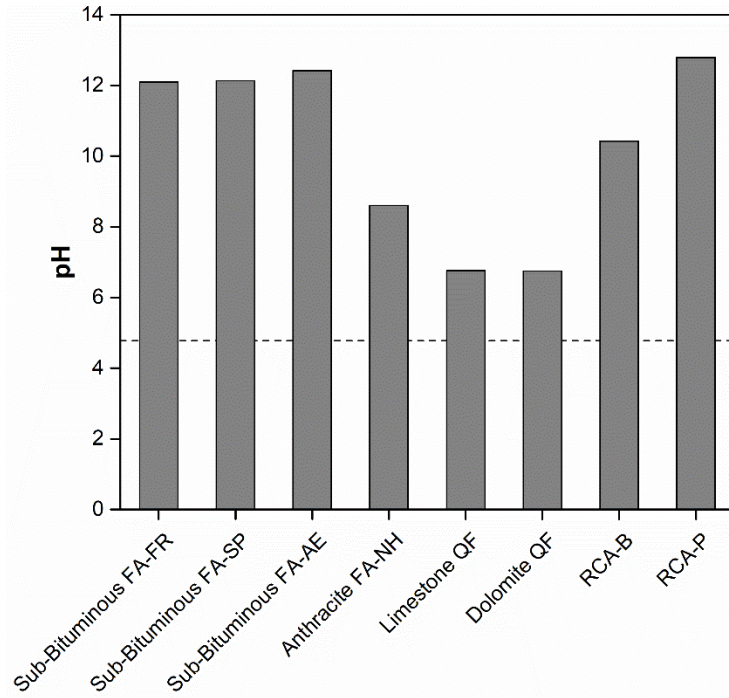


Figure 13. pH of Sunrise coarse CMD following treatment with each industrial byproduct. The dashed line indicates the initial pH of the CMD.

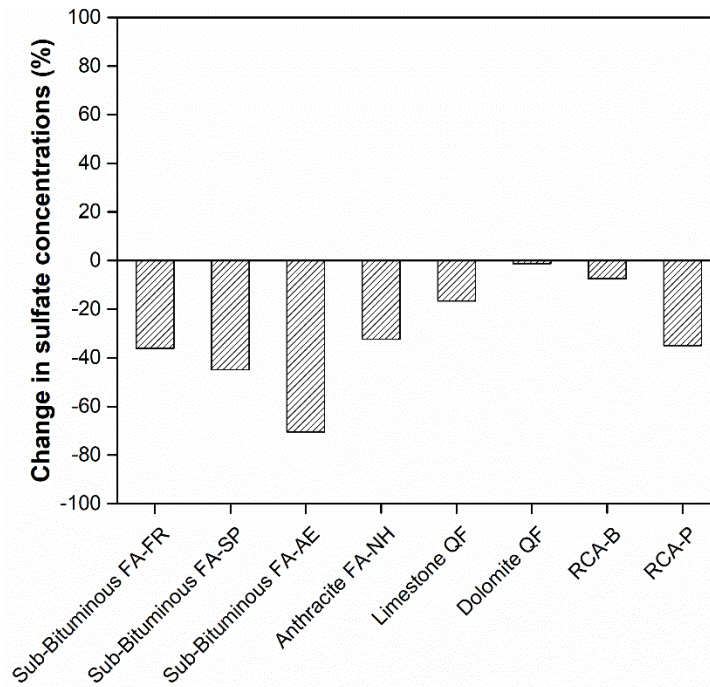


Figure 14. Percent changes in sulfate concentrations of Sunrise coarse CMD following treatment with each industrial byproduct.

Metals removal by industrial byproduct treatment of Sunrise coarse CMD (Figure 15) appeared to have similar trends as observed for Newquist CMD (Figure 9). Though most fly ashes added to the metals pollution of Li, Mo, and V in the Sunrise coarse CMD, these treatments were highly successful (>70% removal) in removing most other metals shown in Figure 15. Other industrial byproducts were able to remove most metals effectively, though not to the same extents as the fly ashes for certain metals.

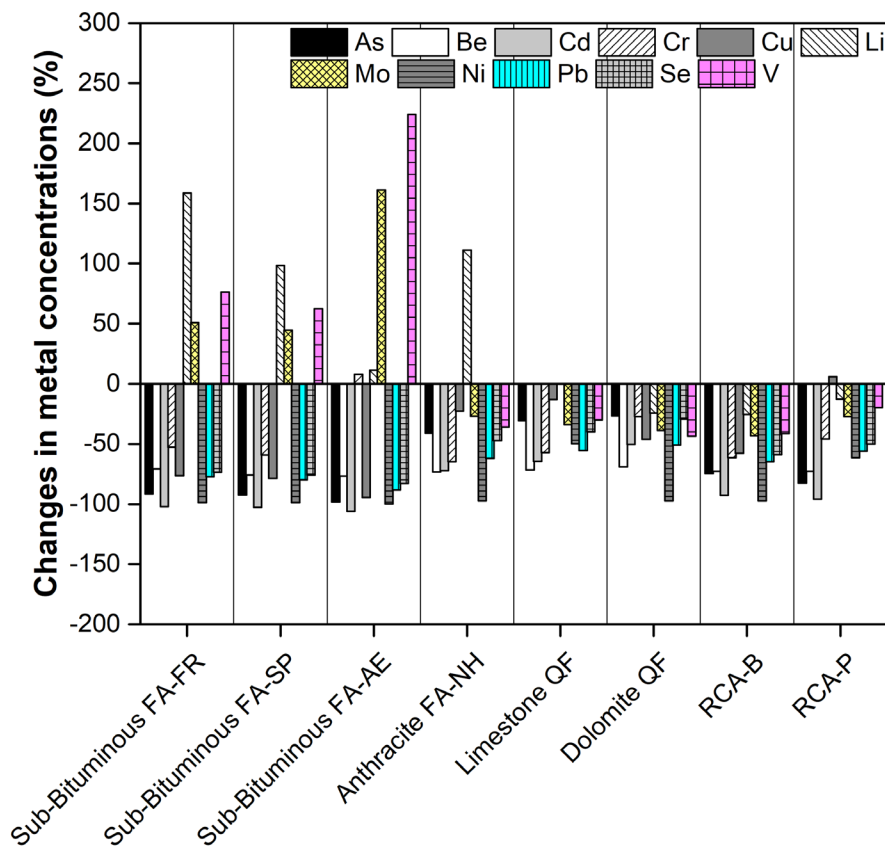


Figure 15. Percent changes in metals concentrations of Sunrise coarse CMD following treatment with each industrial byproduct.

4.4.6 Sunrise fine CMD treatments

As shown in Table 5, Sunrise fine CMD had a near-neutral pH of approximately 6.5, which was increased following treatment with all industrial byproducts (Figure 16). Overall, changes in pH due to treatments were similar to what was observed for Blom Mahaska CMD treatment discussed in section 3.4.1.

Sulfate concentrations either decreased (up to 35%) or increased slightly by up to 10% following treatment of Sunrise fine CMD with industrial byproducts (Figure 17). Together with the initial CMD sulfate concentration of approximately 700 mg/L (Table 5), all final leachates showed sulfate levels well above the MCL.

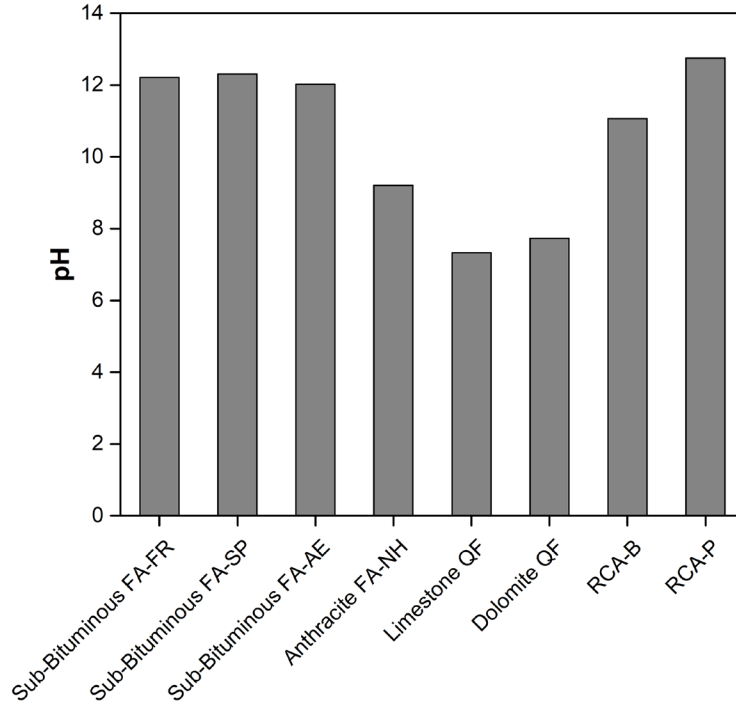


Figure 16. pH of Sunrise fine CMD following treatment with each industrial byproduct. The dashed line indicates the initial pH of the CMD.

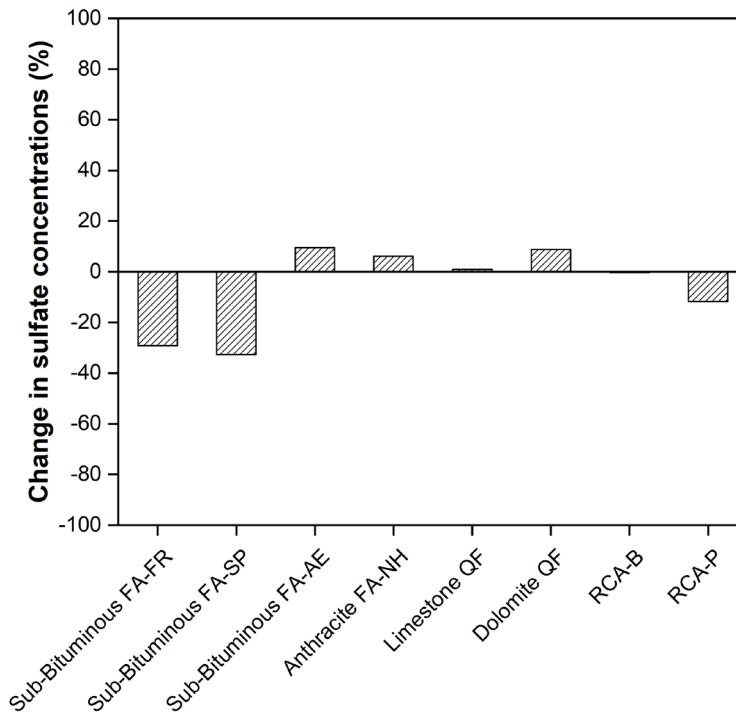


Figure 17. Percent changes in sulfate concentrations of Sunrise fine CMD following treatment with each industrial byproduct.

Metals removal by industrial byproduct treatment of Sunrise fine CMD (Figure 18) appeared to have similar trends as observed for Newquist CMD (Figure 9) and Sunrise coarse CMD (Figure 15). Most fly ashes added to the metals pollution of Li, Mo, and V in the Sunrise fine CMD. Overall, pavement RCA appeared to routinely do relatively well in removing all metals shown in Figure 18.

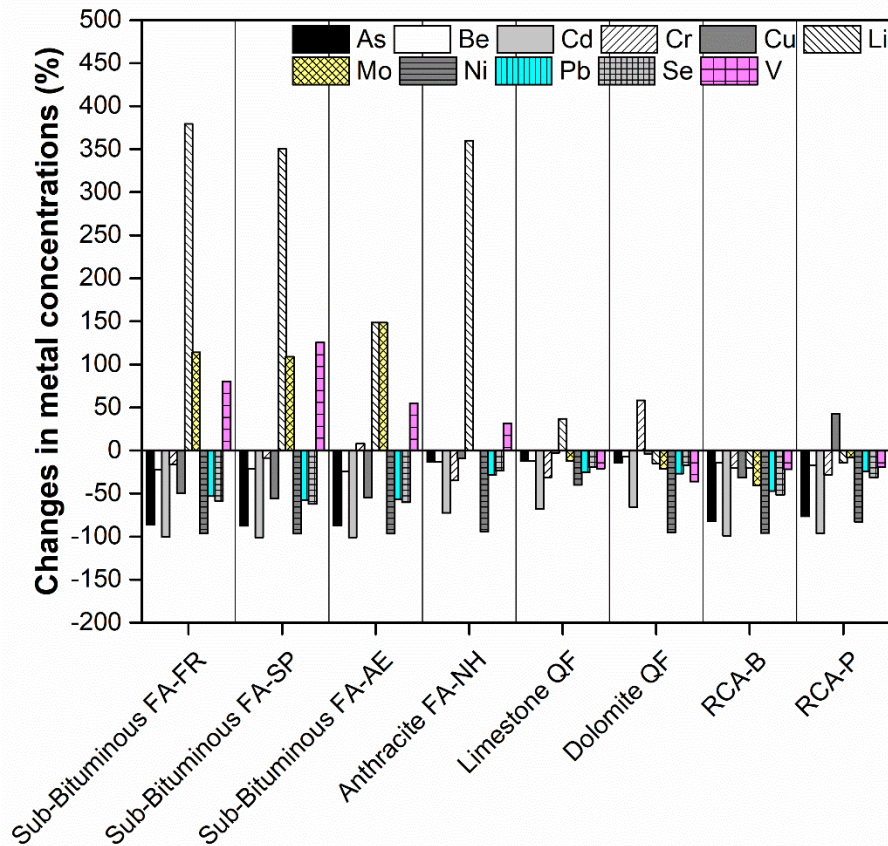


Figure 18. Percent changes in metals concentrations of Sunrise fine CMD following treatment with each industrial byproduct.

4.4.7 Selection of coal mine waste and industrial byproduct materials for CLTs

Based on the assessment on sequential WLTs, Sub-Bituminous coal refuse from Newquist, IA and Bituminous coarse coal refuse from Indiana were selected for CLTs due to their higher leaching potentials of heavy and trace metals. For the treatment purpose, stockpiled Sub-Bituminous fly ash from Cedar Rapids, IA (“Prairie Creek”), limestone quarry fines and RCA from pavement demolition waste were the most efficient in sorbing the metals from CMD. Specifically, these industrial byproducts were the most efficient in removing certain metals (with focus on As, Cd, Pb, and Se because those metals were present in relatively high concentrations in the CMD samples) from CMD in addition to effectively increasing the leachate pH and decreasing the sulfate concentrations. Therefore, Newquist coal and Sunrise coarse coal as well as stockpiled fly ash, limestone quarry fines and RCA-Pavement were used in sequential CLTs in Objective 2 as described below.

5. OBJECTIVE 2: Evaluate the impact of CMD treatment on water quality using a flow-through experimental system

5.1 Column leach test (CLT) conditions

In Objective 2, selected coal refuses and industrial byproducts outlined below were used in CLTs. Three separate setups were tested in this project: (i) single CLTs to determine the baseline leaching behaviors of each material, (ii) sequential CLTs with a coal refuse column mimicking an abandoned mine scenario, and (iii) sequential CLTs with synthetic CMD mimicking an active mine scenario. Of these setups, we focus on the sequential CLTs mimicking abandoned mine scenarios in this Final Report. Data from other CLT experiments are provided in the Appendix.

For the sequential CLTs mimicking abandoned mine scenarios, three columns were assembled in a sequence (Figure 19) following the U.S. EPA 1314. The first column was packed with a coal refuse (i.e., to produce CMD), the second with an industrial byproduct as the treatment column, and the third one was composed of topsoil to determine soil health. The coal mine waste and the treatment columns were 4 inches in diameter and 4 inches in height. The mine waste and the treatment column were prepared at a target porosity of 0.3 ± 0.05 by compacting the materials at optimum moisture contents with a Proctor compaction hammer. Geotextiles were installed at the top and bottom of the compacted fly ash columns to prevent clogging of these fine industrial byproducts which will increase the service life of the system. Two different types of geosynthetics were tested: (i) non-woven geotextile and (ii) woven geotextile. The flow rates through the columns were fixed to 60 mL/hour. The effluent from treatment column was not pumped through the soil column. Instead, gravity flow was induced through the soil column to increase the hydraulic retention time, which was required to investigate the effects of treated CMD on soil quality. Therefore, a large (3 inches in diameter and 12 inches in length) soil column was used with at a higher porosity of 0.5 ± 0.05 . A large column with higher target porosity accommodated three soil sampling locations and ensured adequate permeability. Natural soil was used for soil columns. According to Unified Soil Classification System, the soil was classified as low plasticity silt (ML).

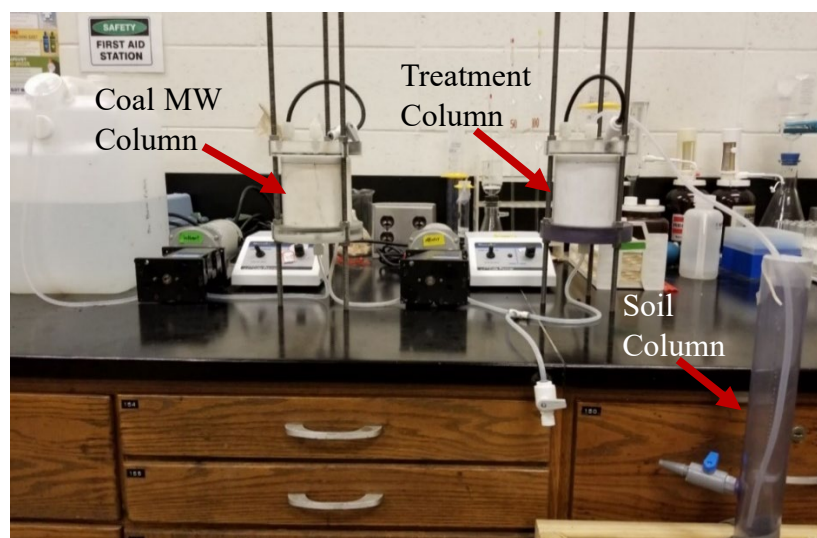


Figure 19. Sequential column leach test setup.

In brief, nanopure water was flushed through the mine waste column to produce CMD. This leachate was pumped through a byproduct column, and its effluent (treated CMD) was then percolated through a soil column to access the environmental impacts of the treated CMD. The sequential CLTs were run non-stop for several days until the treated CMD (byproduct column effluent) showed no change in the removal of toxic metals. Because the amount of coal refuse was finite in the first column, the pollutant load and water chemistry in the CMD produced from the first column decreased over time; as a finite amount of coal mine wastes is expected in abandoned mines, this CLT setup was designed to test how well each treatment may work for such scenarios. A list of the sequential CLTs performed are shown in Table 7. The exact pore volumes and porosities of each packed column in each CLT sequence are shown in Table 8. A 70 mL of effluent solution was collected from each column per day for water quality analysis and the measurement of metal concentrations listed in Table 4. The results reported herein focus on pH, sulfate, and metals concentrations.

Table 7. Sequential CLTs considering simulated CMDs

CLT sequence	COAL WASTE MATERIAL	INDUSTRIAL BYPRODUCT
1	Sub-Bituminous (Newquist, IA)	Limestone quarry (Ames, IA)
2	Sub-Bituminous (Newquist, IA)	RCA from pavement waste (Ames, IA)
3	Sub-Bituminous (Newquist, IA)	Stockpiled Sub-Bituminous fly ash (Cedar Rapids, IA) with woven geotextile
4	Sub-Bituminous (Newquist, IA)	Stockpiled Sub-Bituminous fly ash (Cedar Rapids, IA) with non-woven geotextile
5	Bituminous coarse (Sunrise Coal Mine, IN)	Limestone quarry (Ames, IA)
6	Bituminous coarse (Sunrise Coal Mine, IN)	RCA from pavement waste (Ames, IA)
7	Bituminous coarse (Sunrise Coal Mine, IN)	Stockpiled Sub-Bituminous fly ash (Cedar Rapids, IA) with woven geotextile
8	Bituminous coarse (Sunrise Coal Mine, IN)	Stockpiled Sub-Bituminous fly ash (Cedar Rapids, IA) with non-woven geotextile

Table 8. Pore volume for each of the columns used in the sequential CLTs.

CLT Sequence	Coal Waste Column		Treatment Column		Soil Column		Geotextile Used
	PV (cm ³)	Porosity	PV (cm ³)	Porosity	PV (cm ³)	Porosity	
1	252	0.31	284	0.34	728	0.52	--
2	237	0.25	290	0.35	710	0.51	--
3	212	0.26	217	0.27	710	0.51	Woven
4	214	0.26	231	0.28	710	0.51	Non- Woven
5	214	0.26	259	0.31	702	0.51	--
6	219	0.27	293	0.35	710	0.51	
7	219	0.27	244	0.30	710	0.51	Woven
8	230	0.28	259	0.31	710	0.51	Non- Woven

Note: PV = Pore Volume

5.2 Results for Sub-Bituminous coal waste (Newquist, IA)

5.2.1 pH

CMD from Sub-Bituminous coal waste materials from Newquist, IA had an initial pH ranging from 3.0 to 3.4. Treatment with limestone quarry fines, pavement RCA, and stockpiled Sub-Bituminous fly ash using woven and non-woven geotextile lasted 23, 18, and 21 days, respectively (Figure 20). By the end of each treatment, the treated CMD following the second column had pH values of 7.04, 11.35, 10.7, and 10.4 for limestone quarry fines, pavement RCA, and stockpiled Sub-Bituminous fly ash using woven and non-woven geotextile, respectively. The pH of the soil column stayed mostly constant during the remediation at near-neutral levels regardless of industrial byproduct used in the treatment.

Overall limestone quarry fines performed better in neutralizing the CMD because values stayed closer to neutral pH compared to the other industrial byproduct treatments that led to alkaline effluent pH. It is noteworthy that the neutralization effect took approximately 40 pore volumes for both limestone quarry fines and pavement RCA. On the other hand, the fly ash columns resulted in immediate increases in pH from ~3 in the CMD to >13 in the treatment column effluents, which then decreased over time to a stable pH of ~10.5. The type of geotextile used did not considerably influence the pH obtained in the treated leachate. In addition, soil columns were able to stabilize the pH of the final effluents to approximately 7-8 regardless of the industrial byproduct used.

5.2.2 Sulfate

CMD generated from Newquist Sub-Bituminous coal refuse generally had high initial sulfate levels of ~10,000 mg/L that decreased over time to ~100 mg/L (Figure 21). It is noted that in all experiments, the sulfate concentrations in the CMD decreased significantly by 40 pore volumes with final concentrations as low as 100 mg SO₄/L, suggesting that sulfide minerals were exhausted by then. However, the sulfate concentrations in the treatment columns remained at approximately the same concentrations from 20 pore volumes (or faster) for limestone quarry fines and both fly ash treatments; these concentrations were higher than the CMD concentrations at the same pore volumes. These observations suggest that the limestone quarry fines and fly ash themselves contained overall more sulfide minerals that continued to leach. Therefore, though CMD treatment with all industrial byproducts shown decreased the sulfate concentrations in the initial pore volumes, the treatments appeared to contribute sulfate rather than remove it. Comparatively, pavement RCA was the only material that was able to remove and/or not add sulfate during the experimental period, resulting in lower than MCL levels, even though the removal efficiencies did not appear to be high. The effect of the soil columns was variable in the CLTs, suggesting that sulfate chemistry in these treatment scenarios are affected by other chemicals in the leachates. For sulfate as well as metals, the type of geotextiles used in the fly ash columns did not appear to impact CMD treatment.

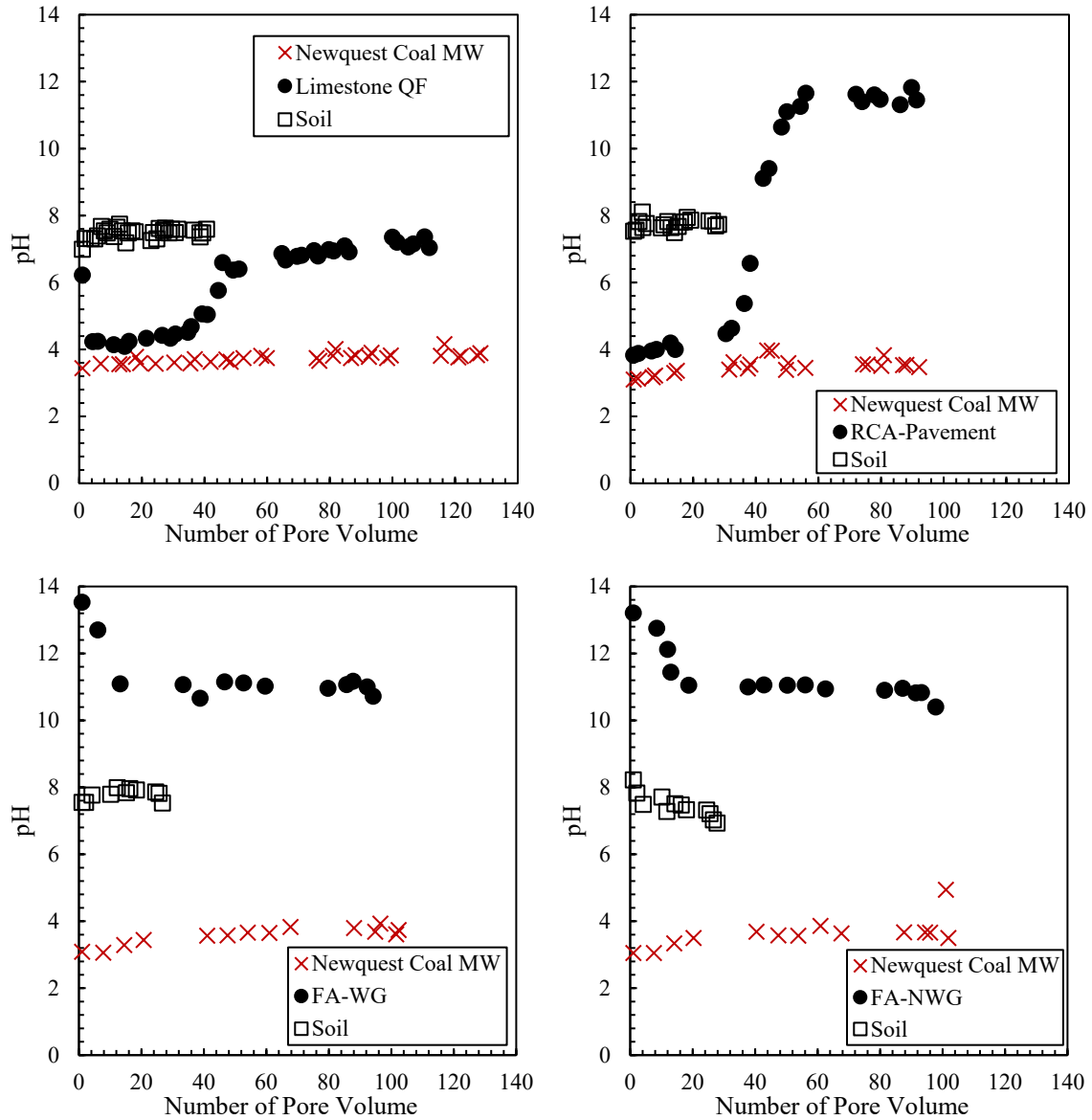


Figure 20. pH measurements for treatment of Sub-Bituminous coal refuse from Newquist, IA (Newquist Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven and non-woven geotextile. Note: FA = Fly ash, WG = Woven Geotextile, NWG = Non-Woven Geotextile.

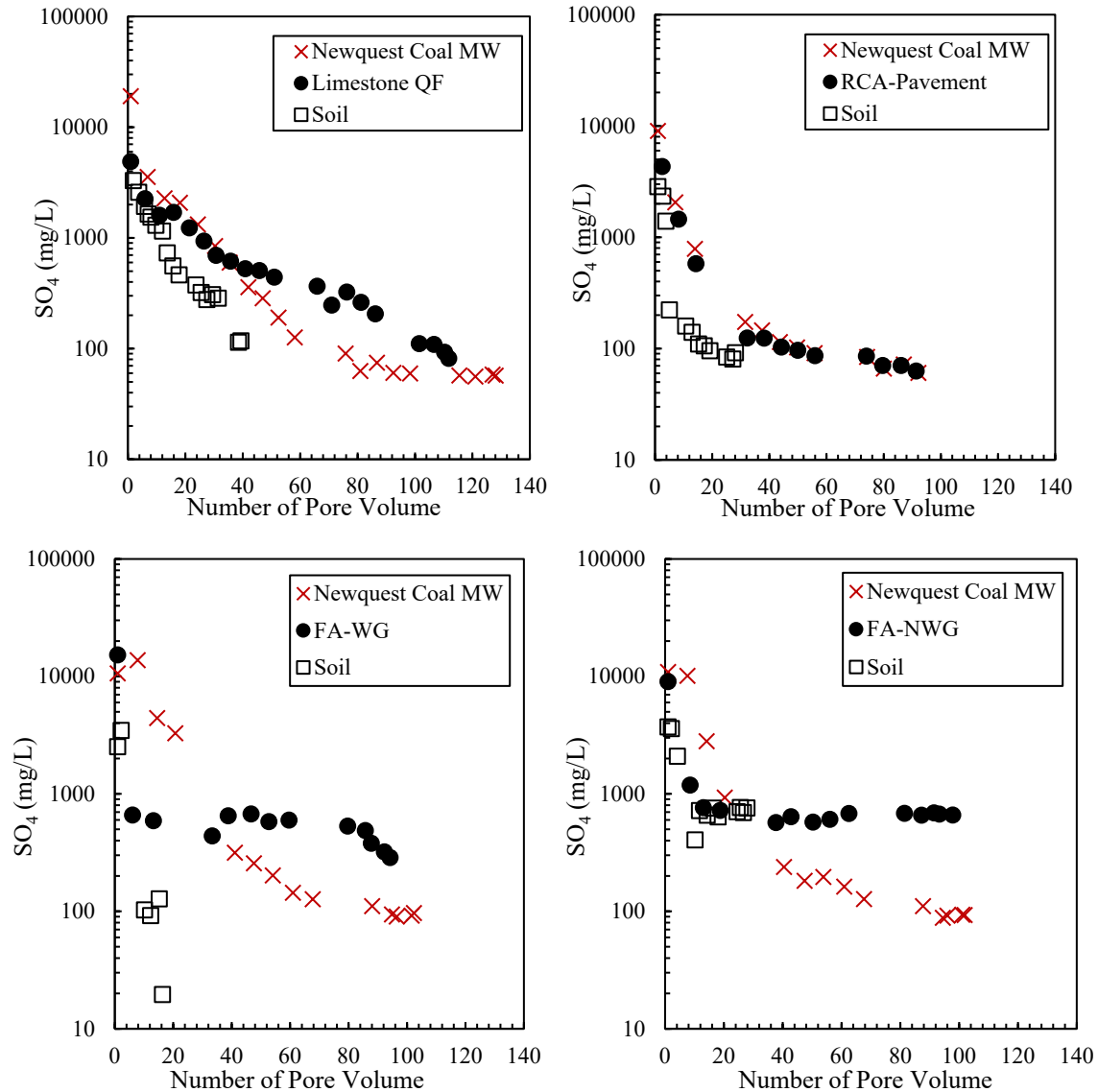


Figure 21. Sulfate measurements for treatment of Sub-Bituminous coal refuse from Newquist, IA (Newquest Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven and non-woven geotextile.

Note: FA = Fly ash, WG = Woven Geotextile, NWG = Non-Woven Geotextile.

5.2.3 Metals

As shown in Figure 22, the initial As concentration in CMD from Newquist coal waste was ~4 mg/L. In general, the CMD concentrations of As decreased with an increase in pore volume, though the concentrations exceeded the MCL even after ~100 pore volumes. Of the treatment materials tested, stockpiled Sub-Bituminous fly ash decreased the CMD concentrations of As most rapidly. However, at larger pore volume of flow, higher concentrations of As were measured for the treatment column indicating the possible leaching of As from fly ash. On the other hand, pavement RCA treatment resulted in consistent decreases in As concentrations in the effluent until ~80 pore volumes. Effluent from the soil column had higher concentrations of As compared to the

fly ash column. Slower flow rates and an accumulation of As from the fly ash column is a possible reason for the observed behavior. In all cases, the concentrations of As in treated and untreated CMD were always higher than the MCL of 0.01 mg/L for As except for pavement RCA. Overall, pavement RCA appeared to be the most effective treatment for As removal from Newquist CMD.

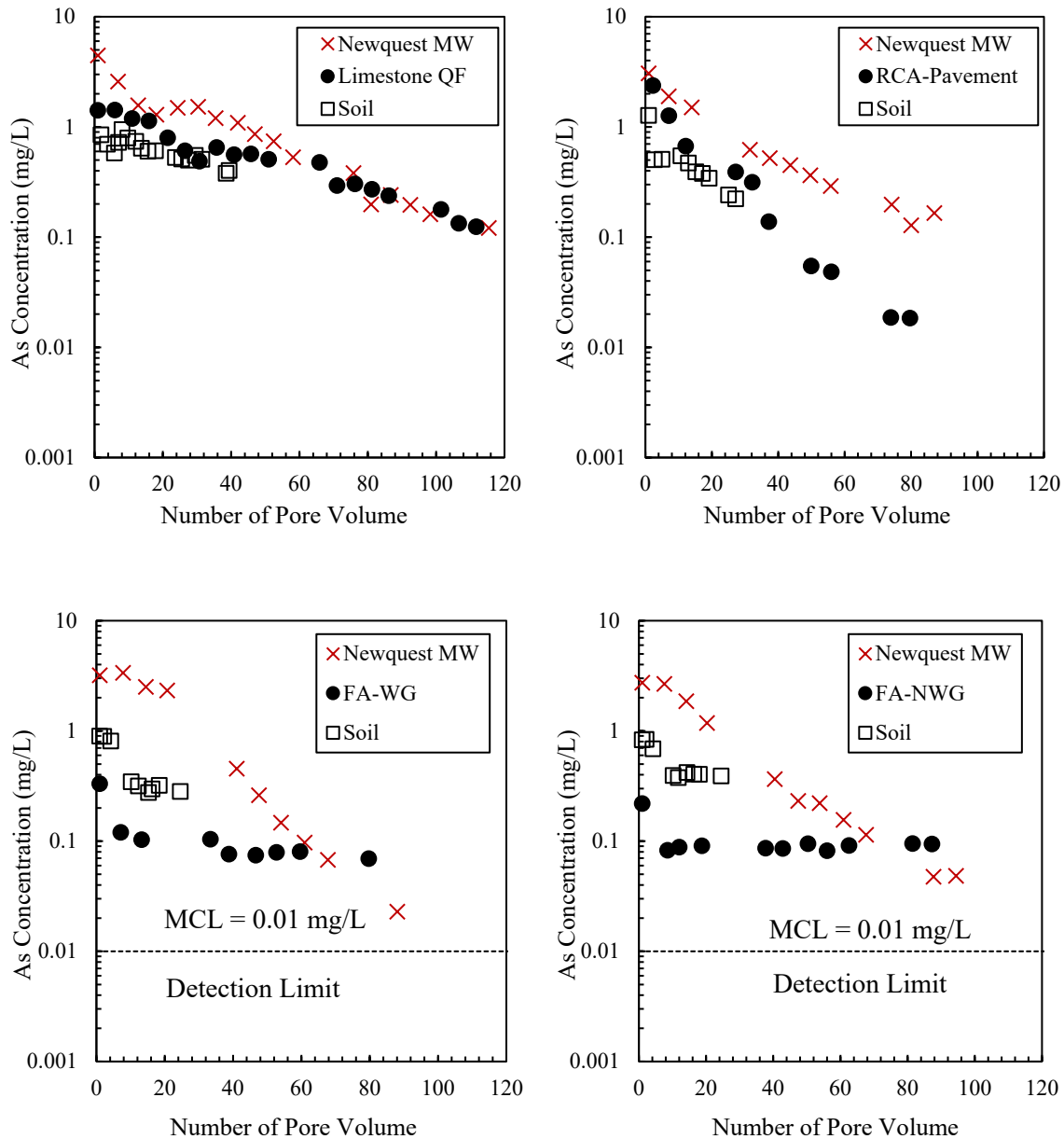


Figure 22. As concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level. The MCL and detection limits for As are both 0.01 mg/L.

As shown in Figure 23, the initial Be concentrations in Newquist CMD was ~ 0.1 mg/L, which gradually decreased with pore volumes. Generally, the CMD Be concentrations fell below the MCL within ~ 50 pore volumes even without treatment. All treatment materials appeared to effectively decrease Be concentrations with fly ash treatment showing the most rapid declines. Therefore, stockpiled Sub-Bituminous fly ash was the most effective for Be removal from CMD.

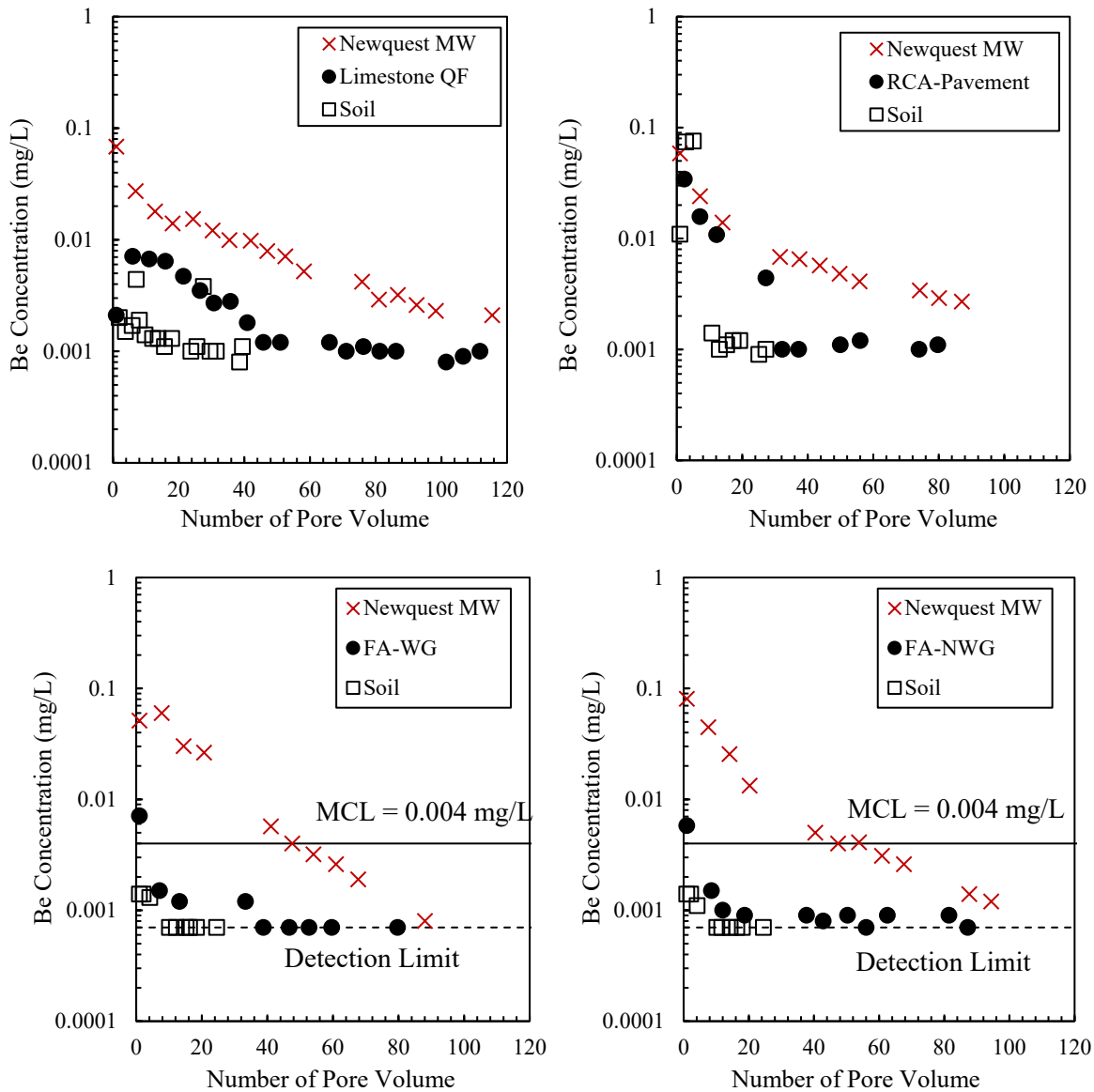


Figure 23. Be concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level.

As shown in Figure 24, CMD had initial Cd concentrations of ~0.3-0.6 mg/L. With an increase in the pore volume of flow, the CMD concentrations of Cd decreased. The overall trends of Cd removal by industrial byproduct treatments appeared to be similar to those observed for Be, in which stockpiled Sub-Bituminous fly ash was the most effective treatment to decrease Cd from CMD.

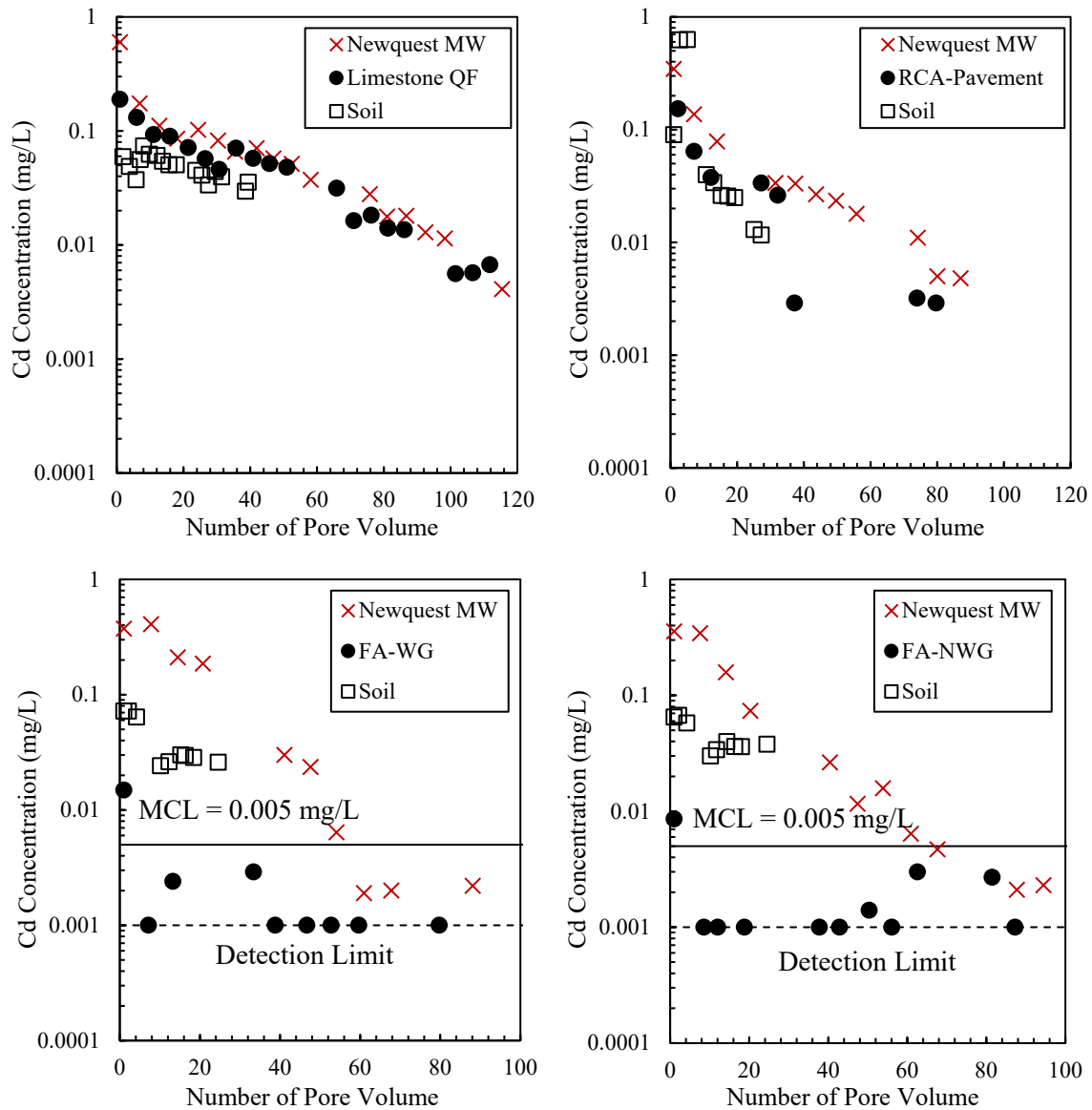


Figure 24. Cd concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level.

As shown in Figure 25, initial Cr concentrations in the CMD were approximately 0.4 mg/L. Though there appeared to be some Cr removal by limestone quarry fines and fly ashes, the Cr levels in the CMD without treatment decreased to below MCL within 5 pore volumes, which was in most cases faster than the industrial byproduct treatment effects. Therefore, none of the materials were deemed significantly effective for Cr removal from CMD.

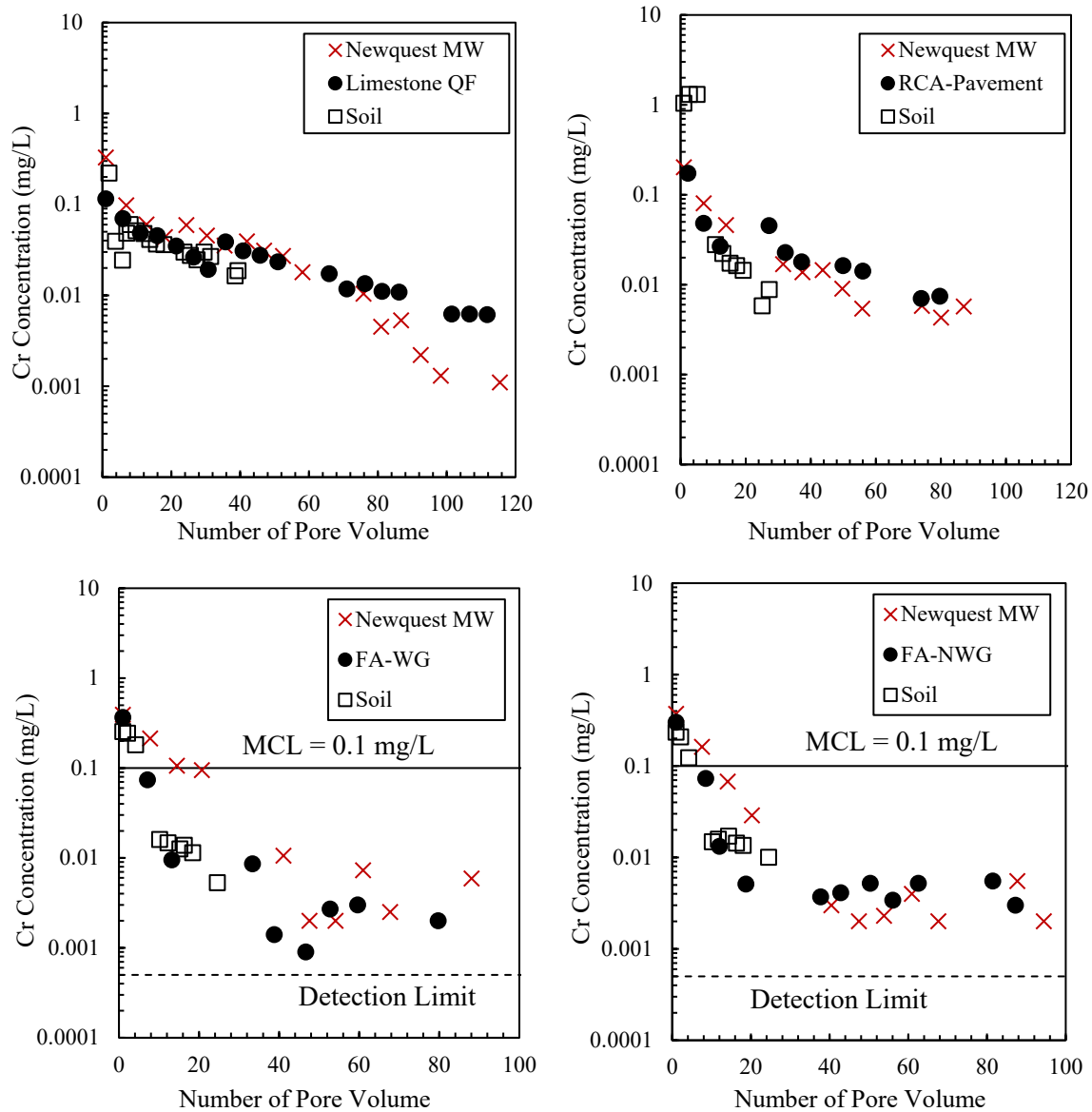


Figure 25. Cd concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level.

As shown in Figure 26, Cu levels in the Newquist CMD were ~1 mg/L for the initial ~20 pore volumes. Though some Cu removal was observed by all industrial byproducts tested, these effects appeared to be variable over time. Overall, treatment with stockpiled Sub-Bituminous fly ash most effectively decreased the CMD concentrations of Cu. However, Cu concentrations in fly ash effluent gradually increased with an increase in flow volume, suggesting that the fly ash's capacity for Cu adsorption was limited. Additionally, it should be noted that the concentrations of Cu in untreated CMD were below the MCL of 1.3 mg/L throughout the test period.

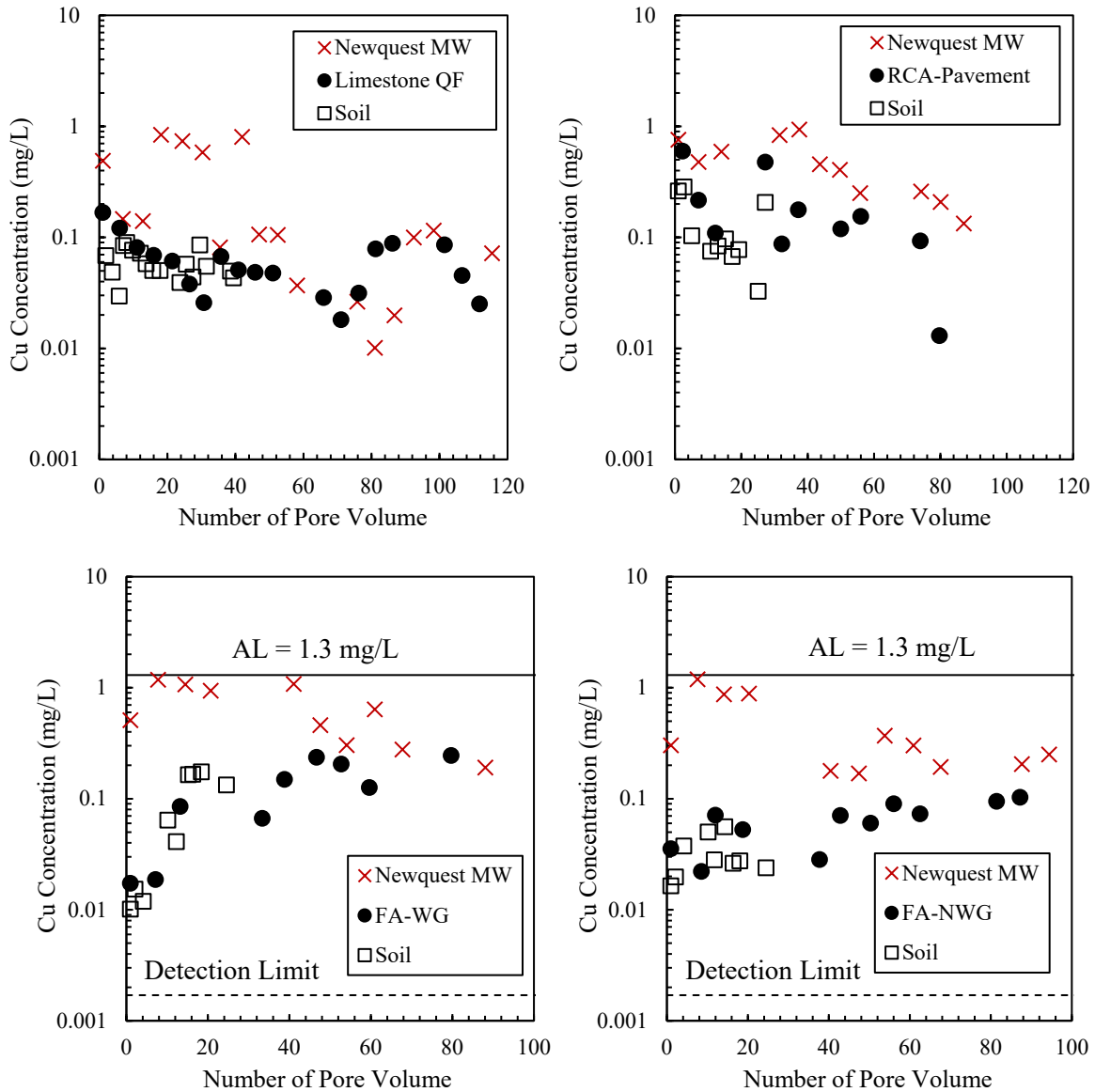


Figure 26. Cu concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, AL = Action Level.

As shown in Figure 27, initial Li concentrations in the Newquist CMD were approximately 5 mg/L, which decreased over time and flow volume. Though some removal was observed with pavement RCA and fly ashes, none of the industrial byproducts tested appeared to be effective for Li removal overall. In fact, treatment with fly ash reduced the CMD concentrations of Li up to the pore volume of 13; however, at higher flow volumes, Li concentrations in treated CMD were higher compared to the ones in untreated CMD.

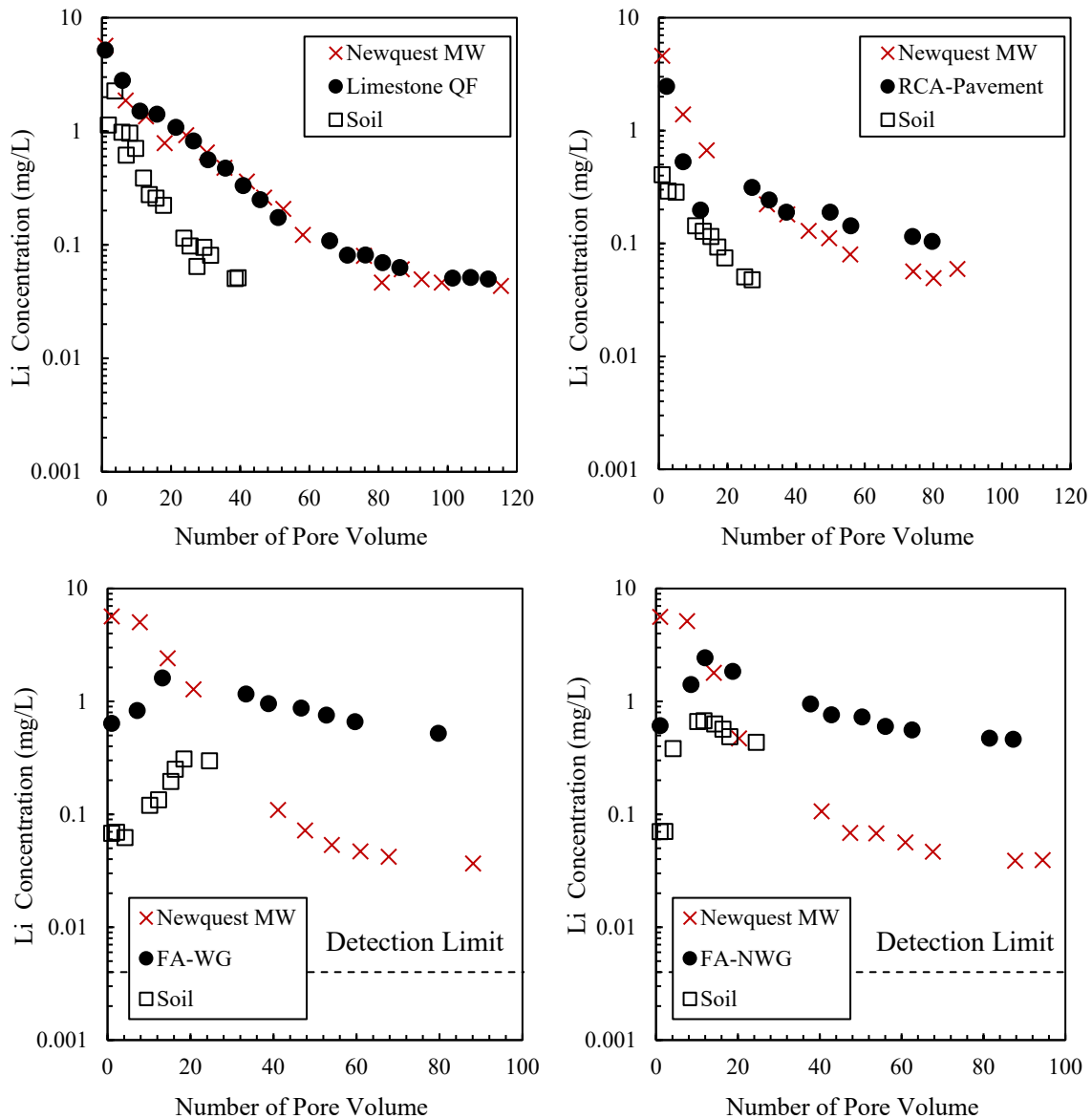


Figure 27. Li concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash. There is no MCL for Li.

As shown in Figure 28, Mo concentrations of ~ 0.5 mg/L in the Newquist CMD was observed in the first pore volume, which decreased with an increase in flow volume. Though limestone quarry fines and fly ashes decreased Mo concentrations in initial pore volumes, their effluent Mo concentrations were higher than that of CMD after ~ 60 pore volumes. These observations suggest that the materials themselves leached Mo. On the other hand, pavement RCA showed only slight decreases in Mo concentration in initial pore volumes, but showed significantly increased Mo removal after ~ 50 pore volumes. As such, pavement RCA appeared to be most effective in Mo removal from CMD.

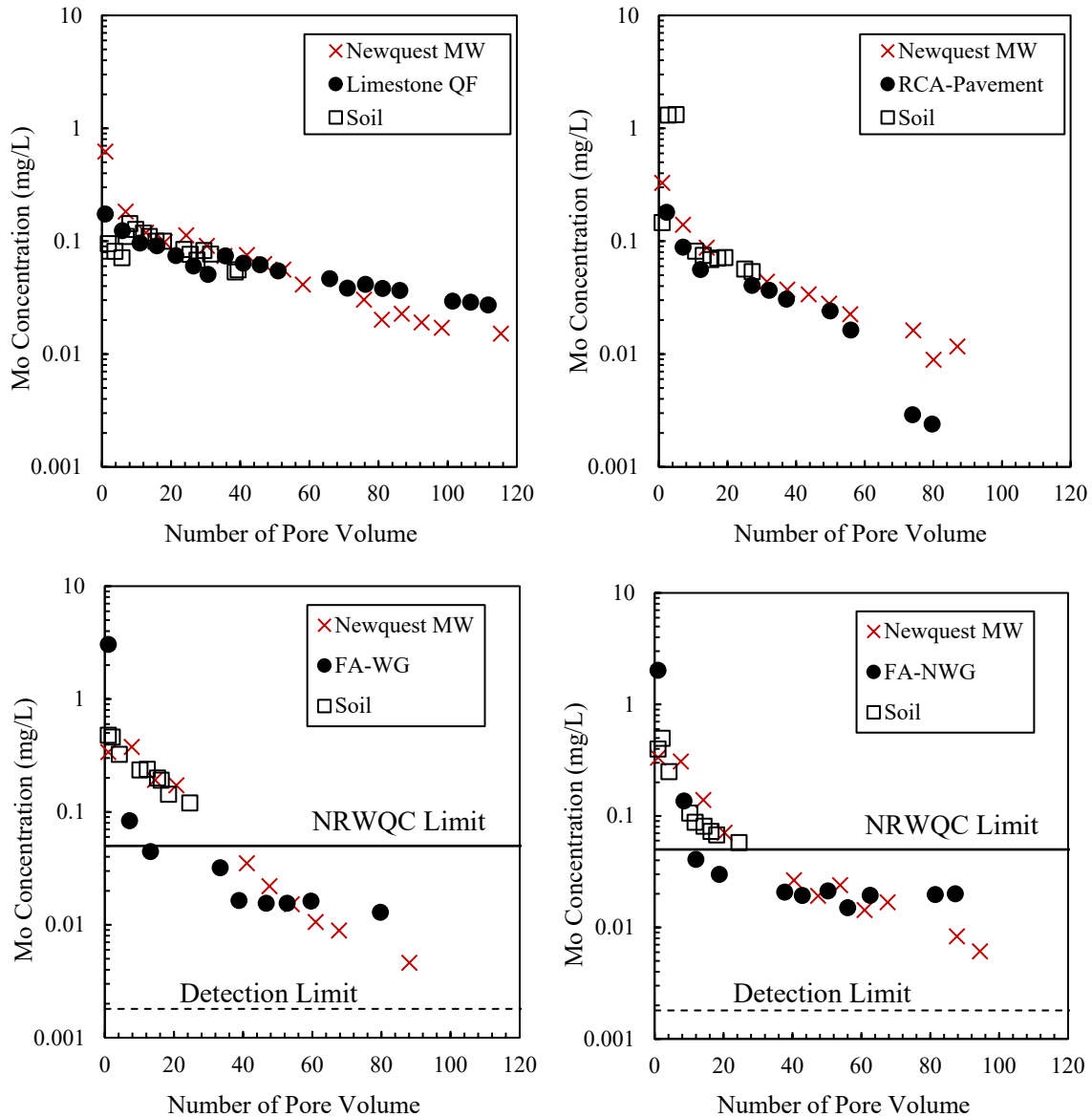


Figure 28. Mo concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, NRWQC = National Recommended Water Quality Criteria.

As shown in Figure 29, initial Ni concentrations in Newquist CMD were ~10 mg/L, which decreased with increased flow through the column. All byproducts appeared to effectively remove Ni to varying degrees. Though fly ash treatment resulted in immediate removal of Ni in the initial pore volumes, Ni concentrations slightly increased in fly ash effluent with an increase in flow volume. On the other hand, pavement RCA treatment started with less Ni removal but showed significant removal with increased flows, suggesting that pavement RCA is the most effective longer-term treatment material for Ni.

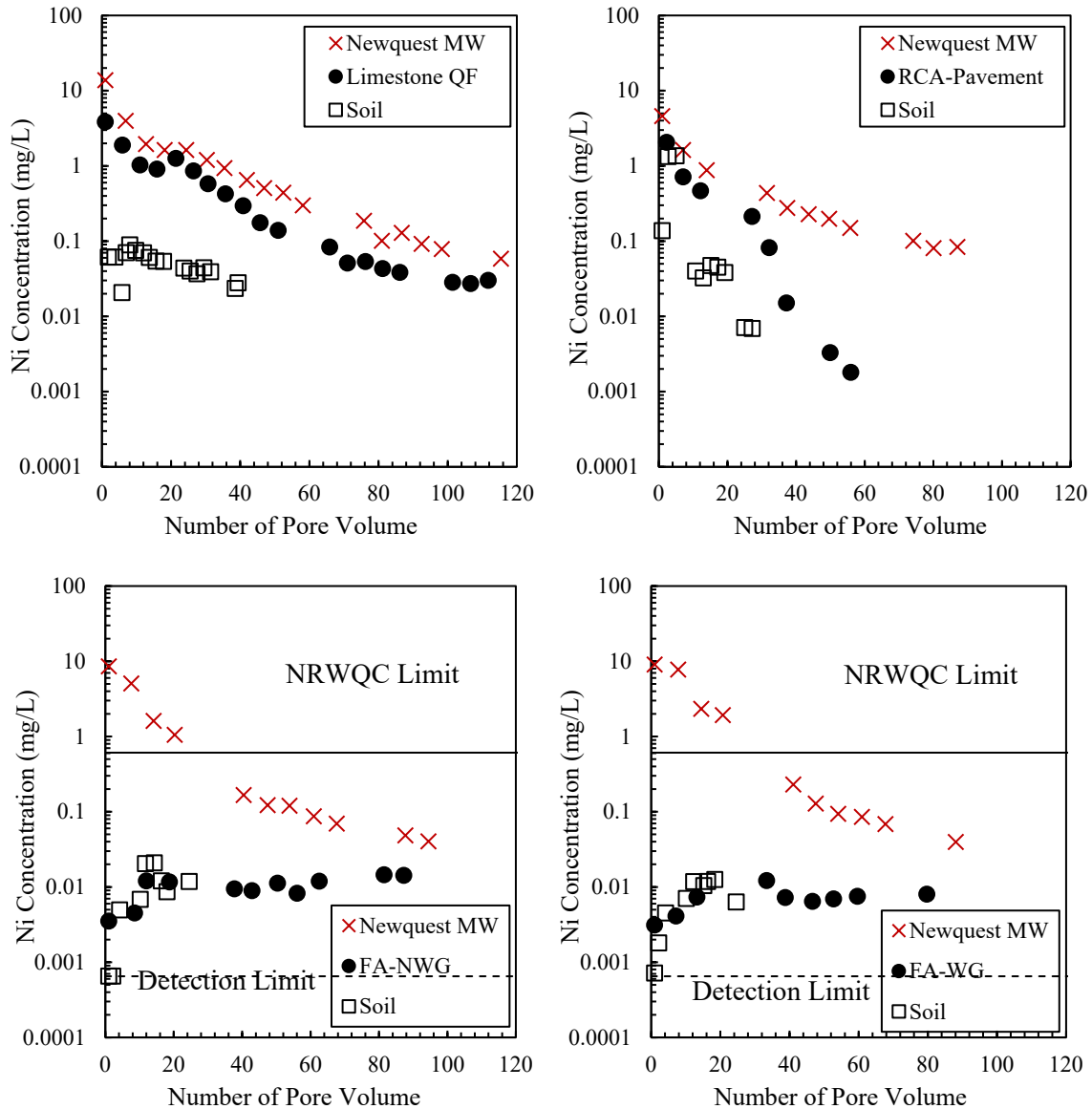


Figure 29. Ni concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, NRWQC = National Recommended Water Quality Criteria.

As shown in Figure 30, initial Pb concentrations in Newquist CMD was ~1 mg/L with concentrations decreasing as flow volumes increased. The treatment trends by the industrial byproducts were similar as those observed for Mo. Overall, pavement RCA appeared to be the most effective material for Pb removal from CMD.

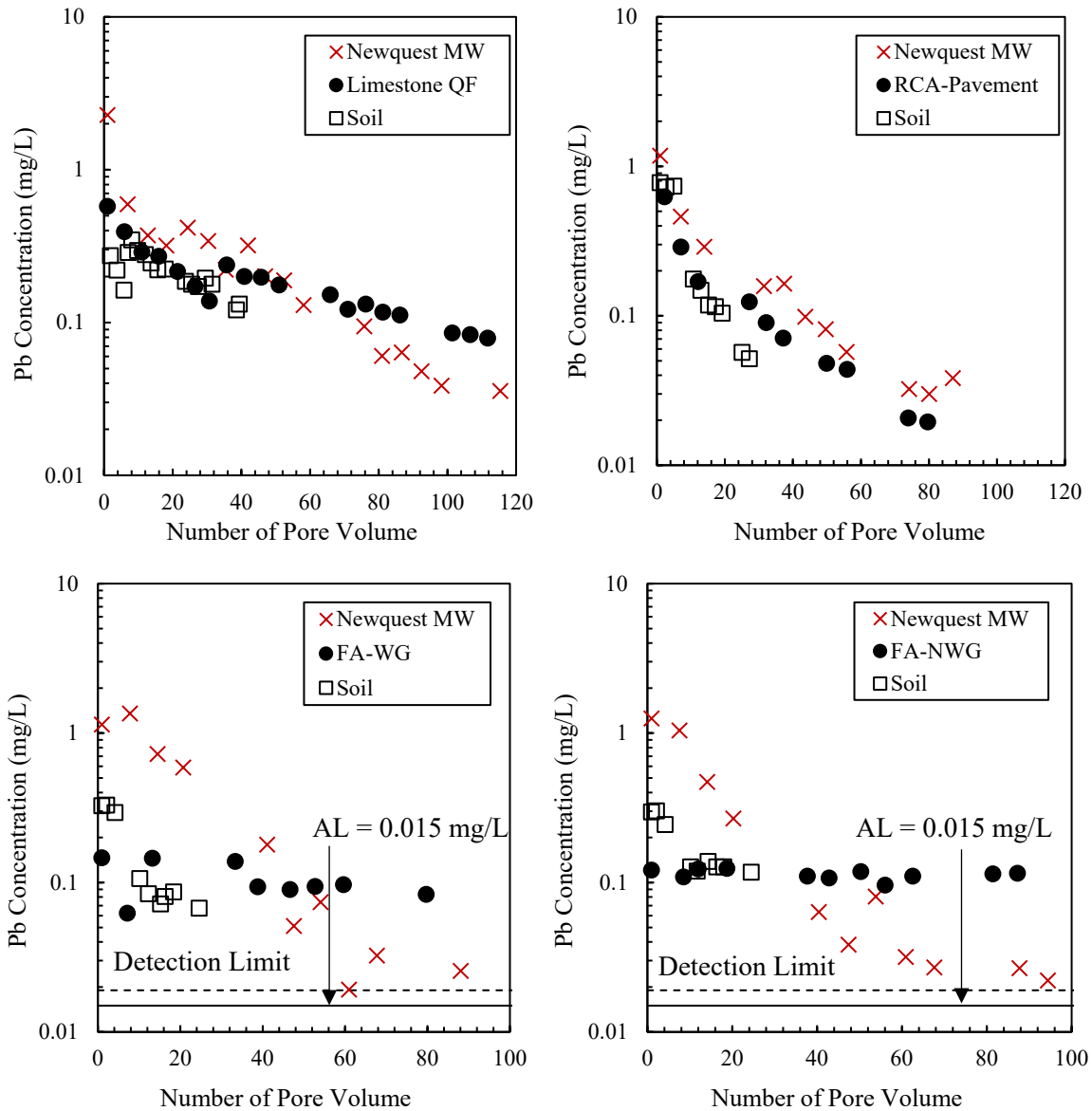


Figure 30. Pb concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, AL = Action Level.

As shown in Figure 31, initial Se concentrations in Newquist CMD were ~8 mg/L and decreased over increasing flow volumes. Overall, the treatment trends were similar as observed for Mo and Pb, in which limestone quarry fines and fly ash appeared to be sources of Se input in later pore volumes. Overall, pavement RCA was the most effective material for Se removal from Newquist CMD.

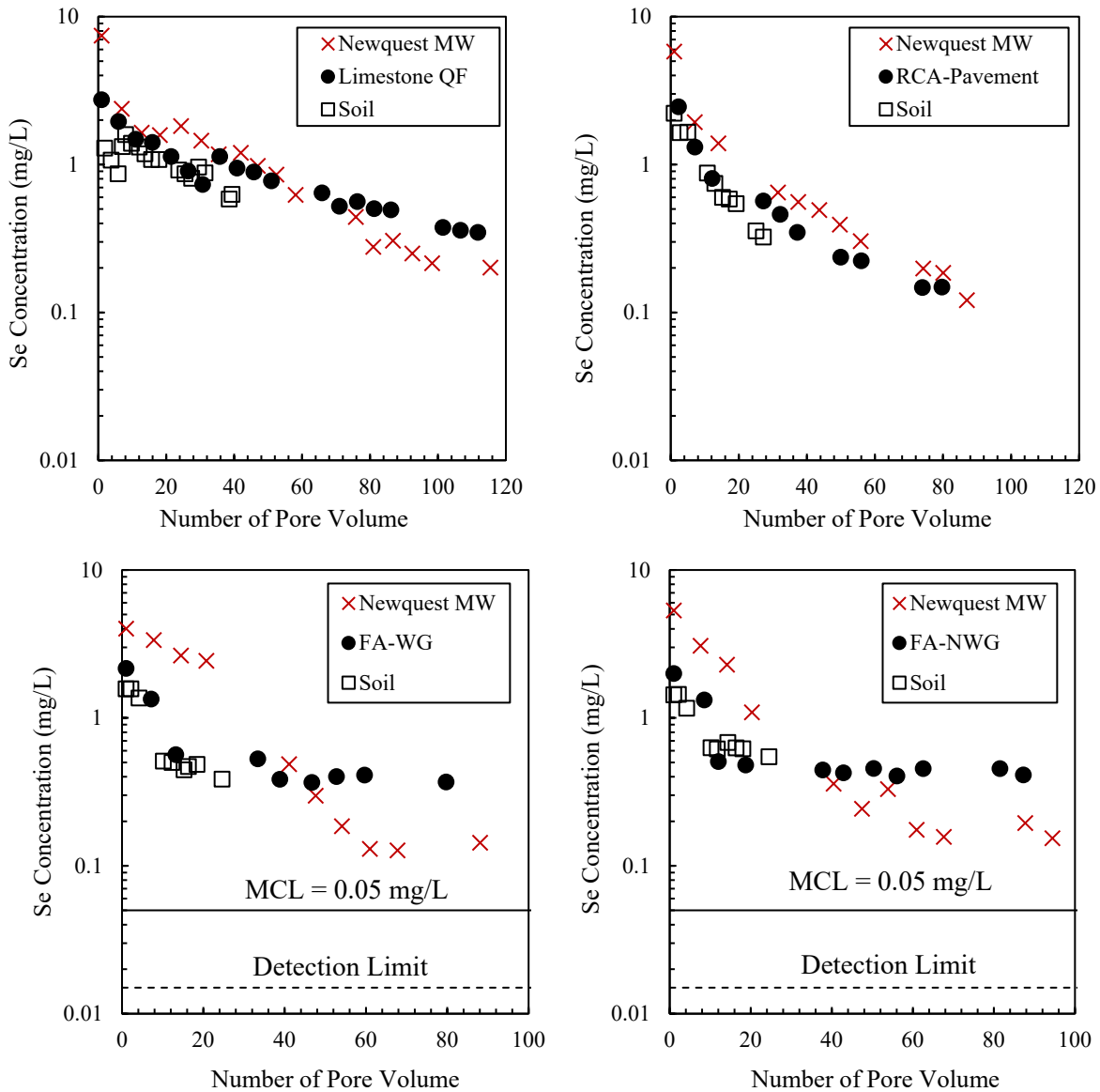


Figure 31. Se concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level.

As observed in Figure 32, V concentrations were ~ 0.1 mg/L in the first pore volume of Newquist CMD with subsequent pore volumes leading to decreased V levels. Though limestone quarry fines treatment resulted in slight decreases in V concentrations from the CMD in the initial pore volumes, V concentrations in the treatment effluent were higher than the untreated CMD after ~ 50 pore volumes. Similarly, fly ash treatment resulted in higher V concentrations compared to untreated CMD at all sampling times. These observations suggest that limestone quarry fines and fly ashes both leach a significant amount of V. Overall, pavement RCA appeared to be the most effective treatment material for V removal from CMD.

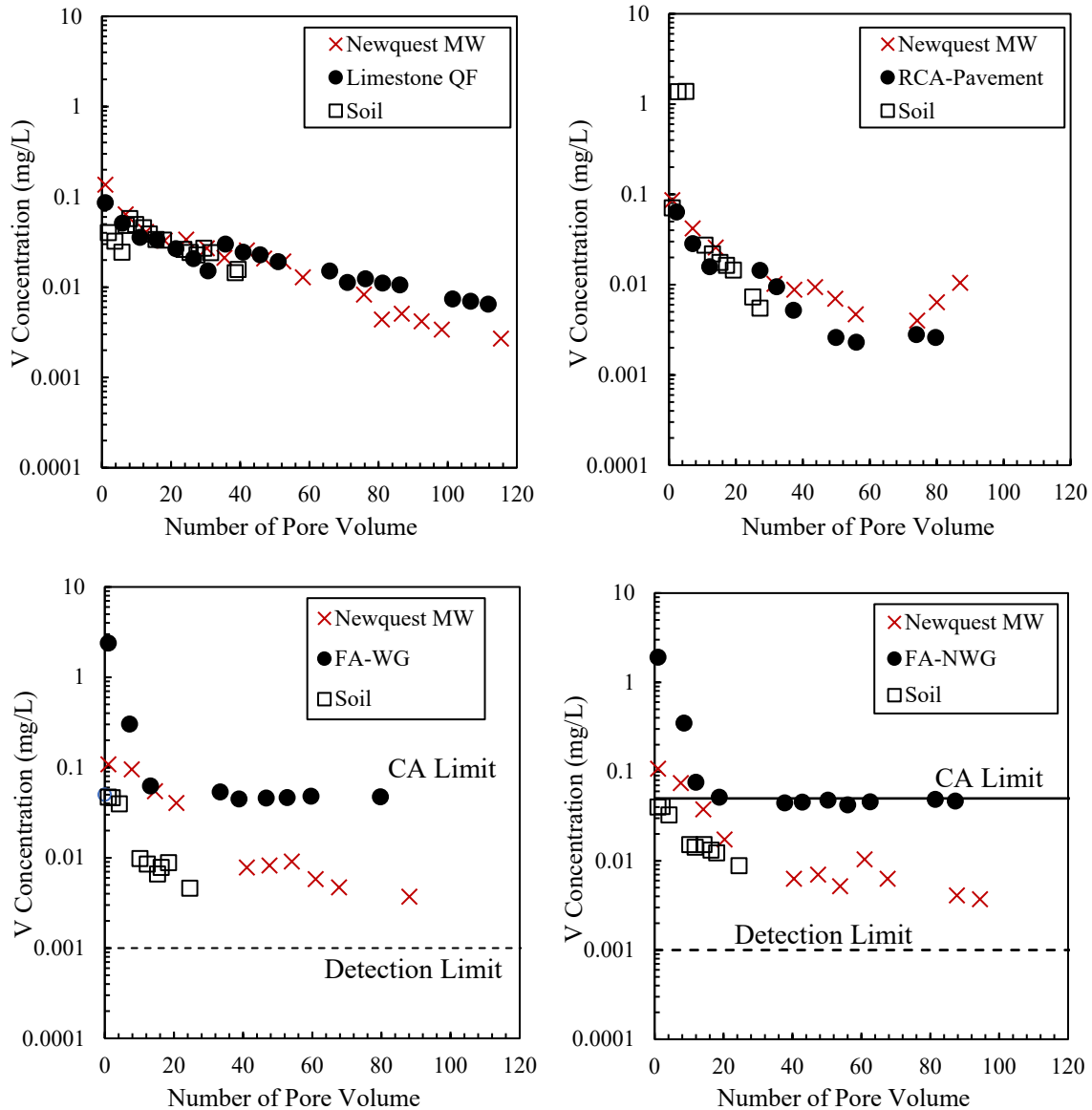


Figure 32. V concentrations for the treatment of Sub-Bituminous coal refuse from Newquist, IA with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash.

5.3 Results for Bituminous coarse coal waste (Sunrise coal mine, IN)

5.3.1 pH

CMD from Bituminous coarse coal waste from Sunrise Coal Mine, IN had an initial pH of ~3 prior to remediation (Figure 33). Treatment with limestone quarry fines, pavement RCA, and fly ash lasted 15, 18, and 18 days, respectively. The pH of the CMD increased within 50 pore volumes, which was likely due to slow exhaustion of sulfide minerals.

The pH trends with industrial byproduct treatments of Sunrise coarse CMD were similar to those observed for Newquist CMD. Limestone quarry fines increased the pH to near-neutral, whereas pavement RCA and fly ash increased the pH to very alkaline levels that were corrosive. The soil column effluents had consistently near-neutral pH in all treatment scenarios. Overall, limestone quarry fines were the most effective material for pH neutralization of Sunrise coarse CMD as it resulted in stable, near-neutral pH.

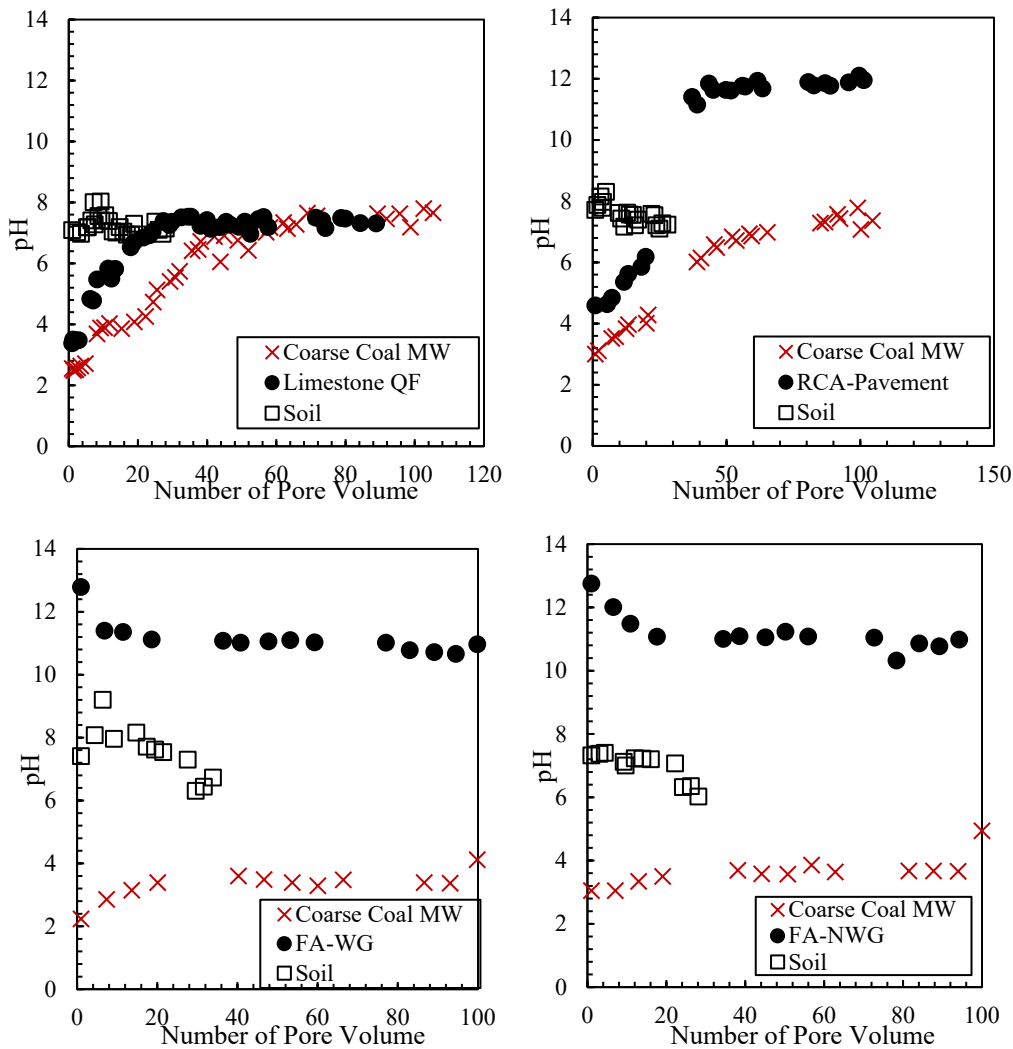


Figure 33. pH measurements for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG).

5.3.2 Sulfate

Sulfate concentrations in the CMD from Sunrise coarse coal waste were initially high (~10,000 mg/L) and decreased with flow volume to ~300 mg/L. The industrial byproducts appeared to have limited effect on sulfate concentrations for this CMD, especially after the first 20 pore volumes. Because the decreasing effects of the materials in the initial pore volumes were all small, it was difficult to determine which industrial byproduct did best at sulfate removal from CMD. For pH, sulfate, and metals, the type of geotextiles used in the fly ash columns did not appear to impact CMD treatment.

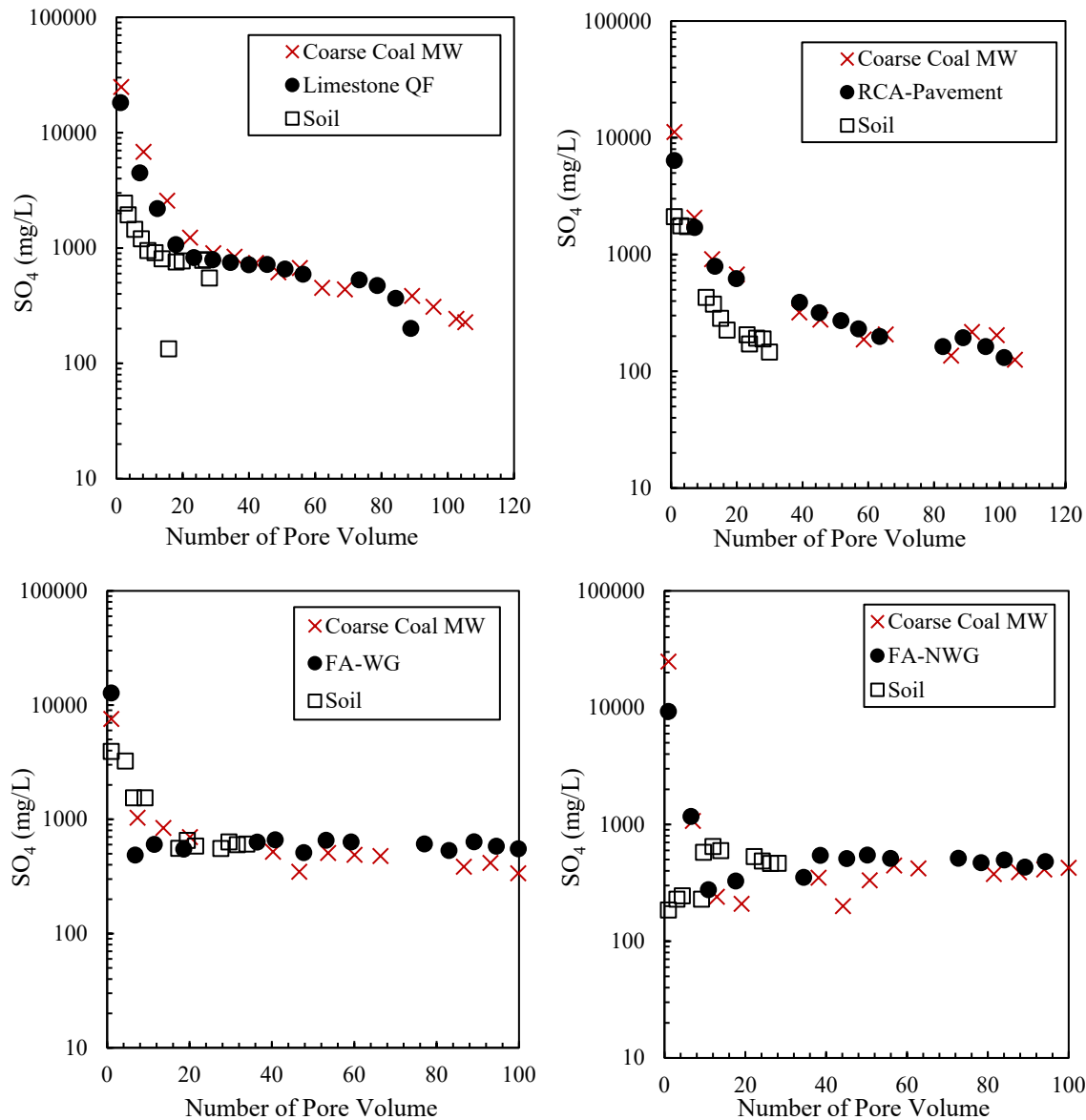


Figure 34. Sulfate measurements for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG).

5.3.3 Metals

As shown in Figure 35, initial As concentrations in the Sunrise coarse CMD were ~10 mg/L, which decreased with increasing pore volumes. Though all industrial byproduct treatments tested showed removal of As, the results pointed to the stockpiled Sub-Bituminous fly ash being the most rapidly and consistently effective material for As removal from CMD.

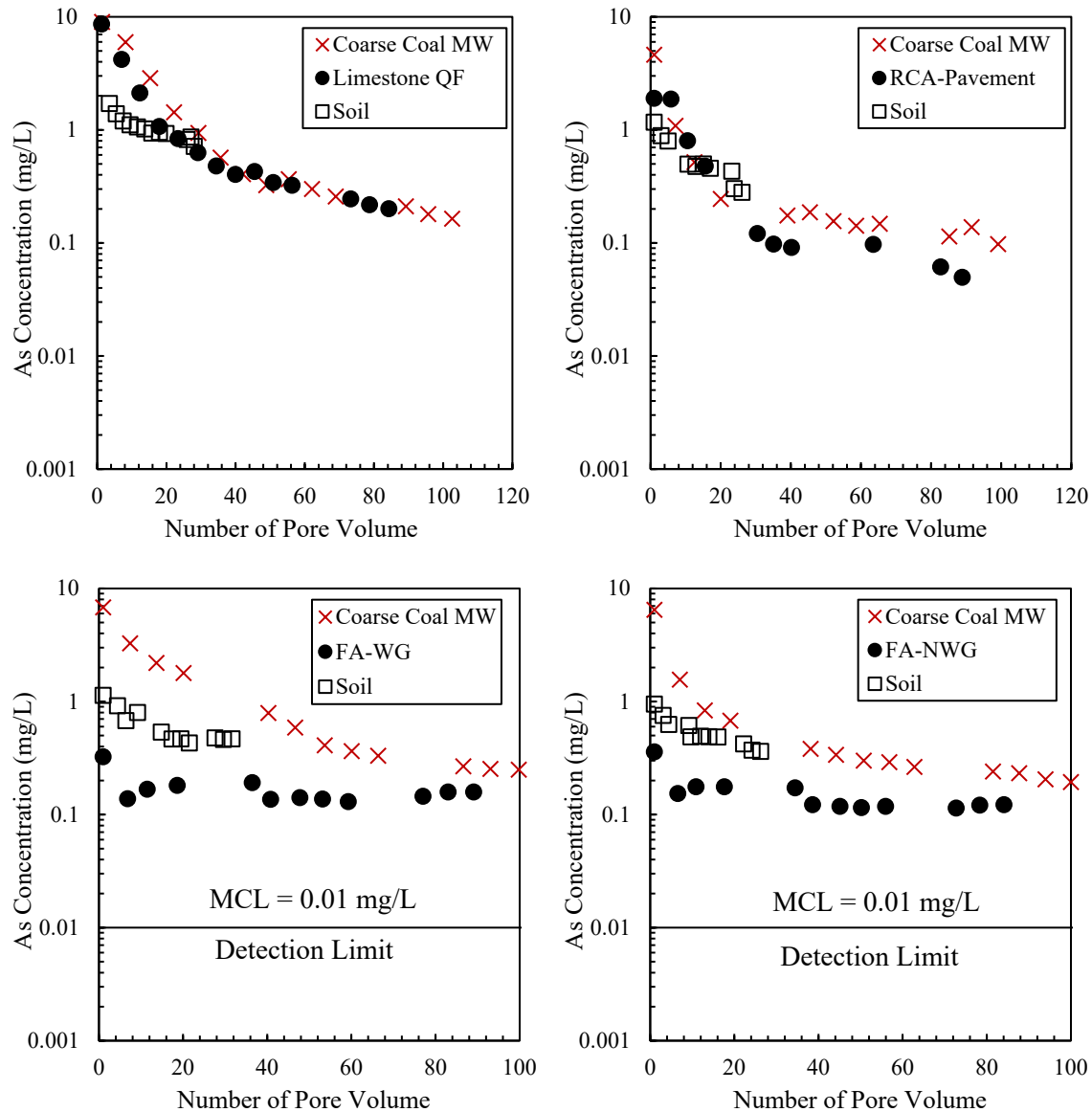


Figure 35. As concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level. The MCL and detection limit for As are both 0.01 mg/L.

As shown in Figure 36, Be concentrations were initially ~ 0.1 mg/L in the Sunrise coarse CMD and decreased to below MCL within 60 pore volumes. Though all materials tested showed significant decreases in Be concentrations, it appeared that pavement RCA treatment was the most effective for Be removal from CMD.

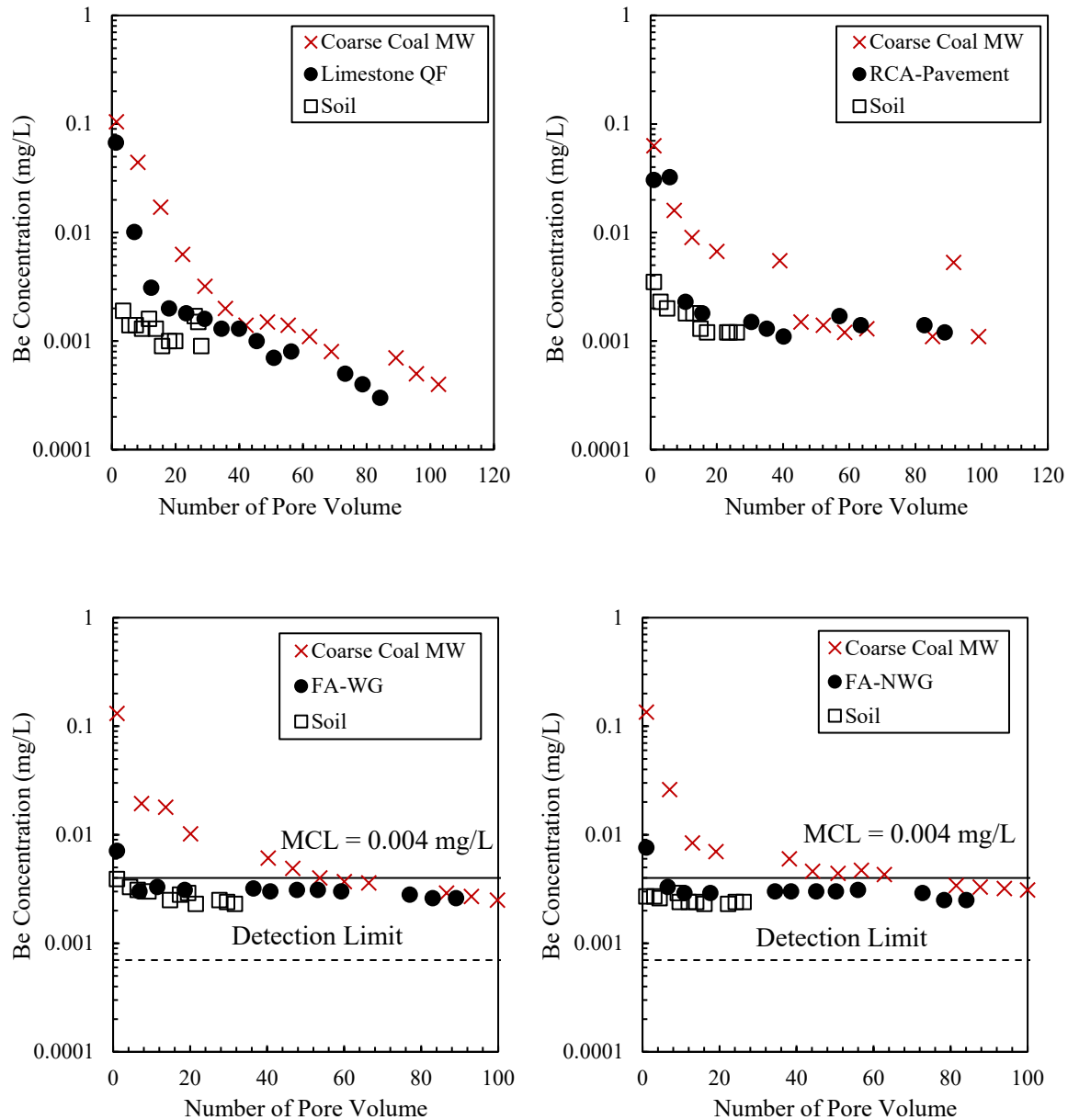


Figure 36. Be concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level.

As shown in Figure 37, Cd concentrations started at ~2 mg/L in Sunrise coarse CMD and decreased to slightly above MCL over time. Limestone quarry fines and fly ash appeared to be effective materials for Cd removal; however, stockpiled Sub-Bituminous fly ash treatment showed the most rapid and consistent removal of Cd.

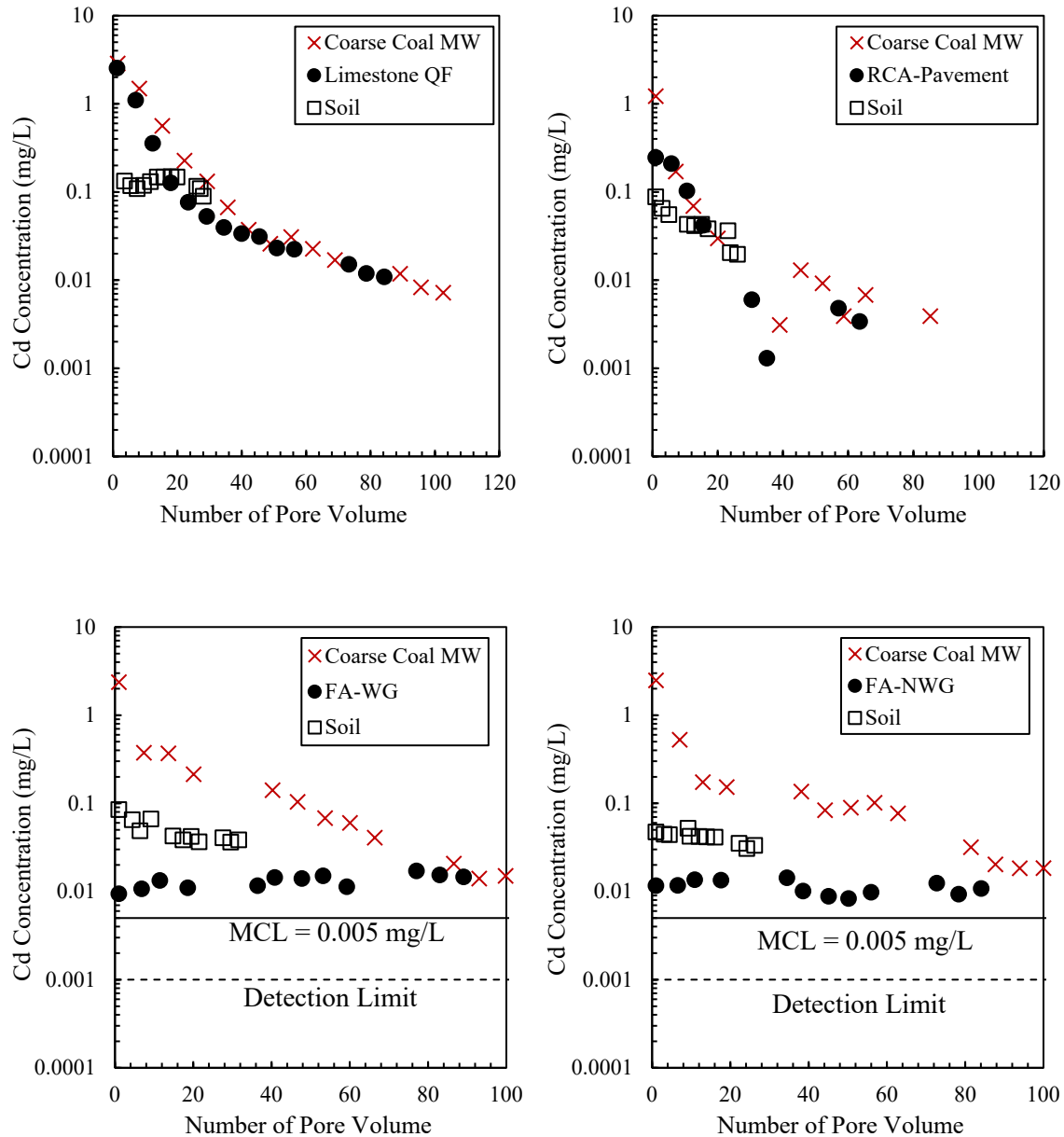


Figure 37. Cd concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level.

As shown in Figure 38, Cr concentrations in Sunrise coarse CMD started at ~1 mg/L and rapidly decreased to below MCL within 20 pore volumes in most of the CLTs. Though all materials showed varying degrees of Cr removal, the results indicated that the stockpiled Sub-Bituminous fly ash was the most effective material for Cr treatment for this CMD.

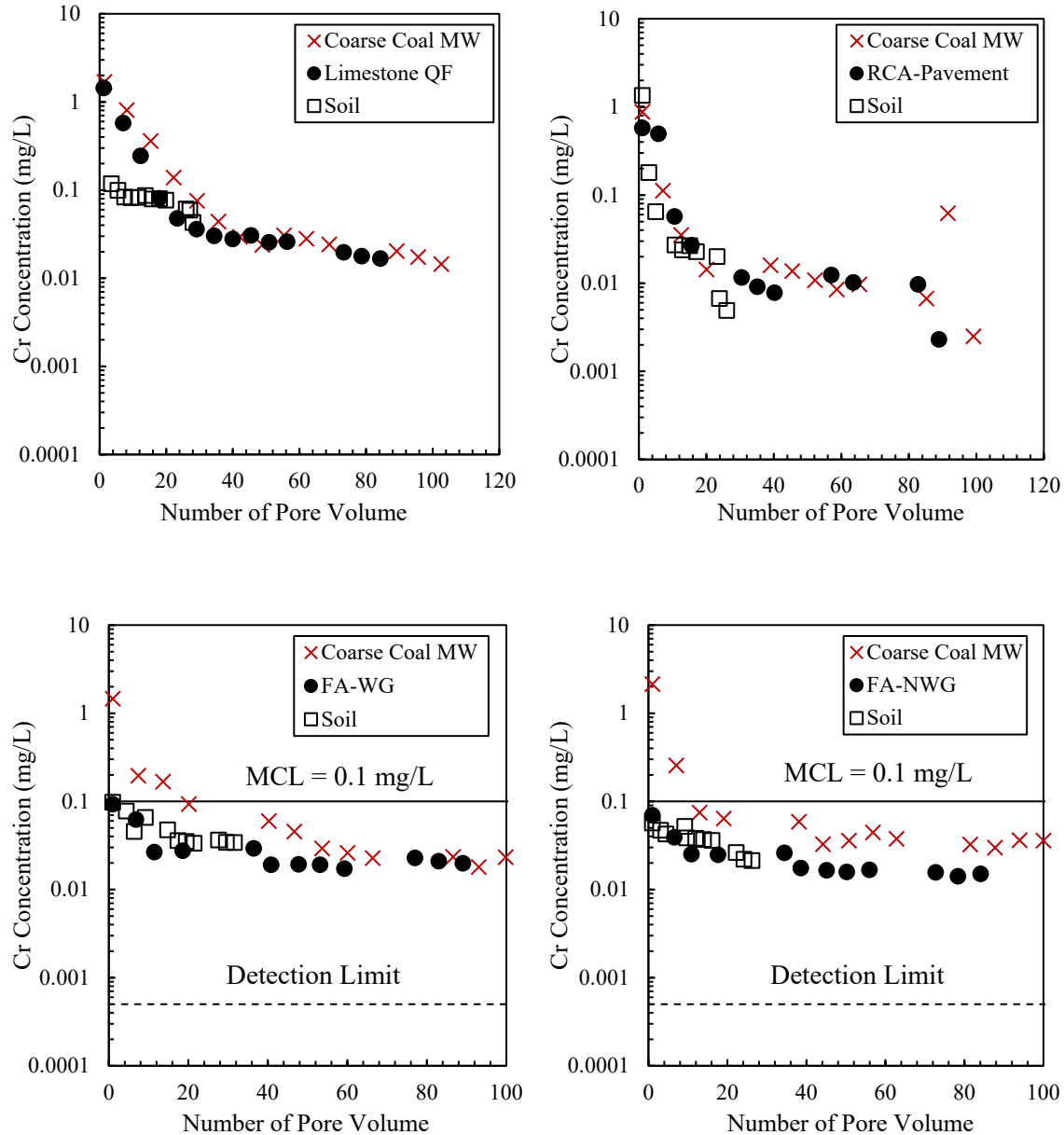


Figure 38. Cr concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level.

As shown in Figure 39, Cu concentrations in the Sunrise coarse CMD varied throughout the CLTs. Overall, though all materials appeared to result in some Cu removal, treatment with stockpiled Sub-Bituminous fly ash seemed to result in rapid and consistent decrease in Cu concentrations in this CMD.

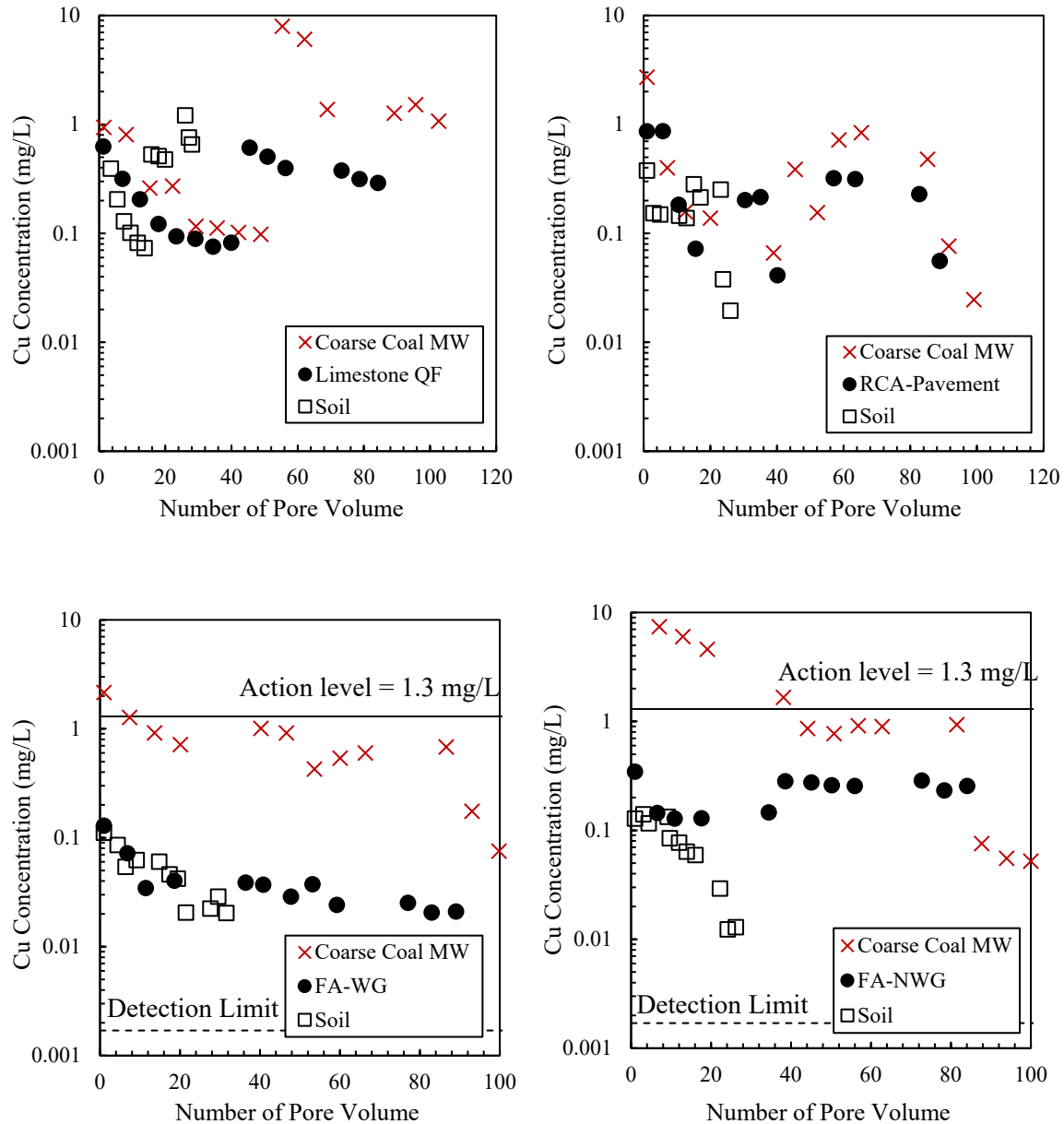


Figure 39. Cu concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash.

As shown in Figure 40, Li concentrations in Sunrise coarse CMD started at ~2 mg/L and decreased rapidly to below 0.1 mg/L. Fly ash and pavement RCA treatments appeared to result in higher Li concentrations in the treatment effluent compared to untreated CMD, suggesting that these materials lead to Li leaching. Though limestone quarry fines removed some Li in initial pore volumes, the removal efficiency seemed low. Therefore, none of the materials were suitable for Li removal from this CMD.

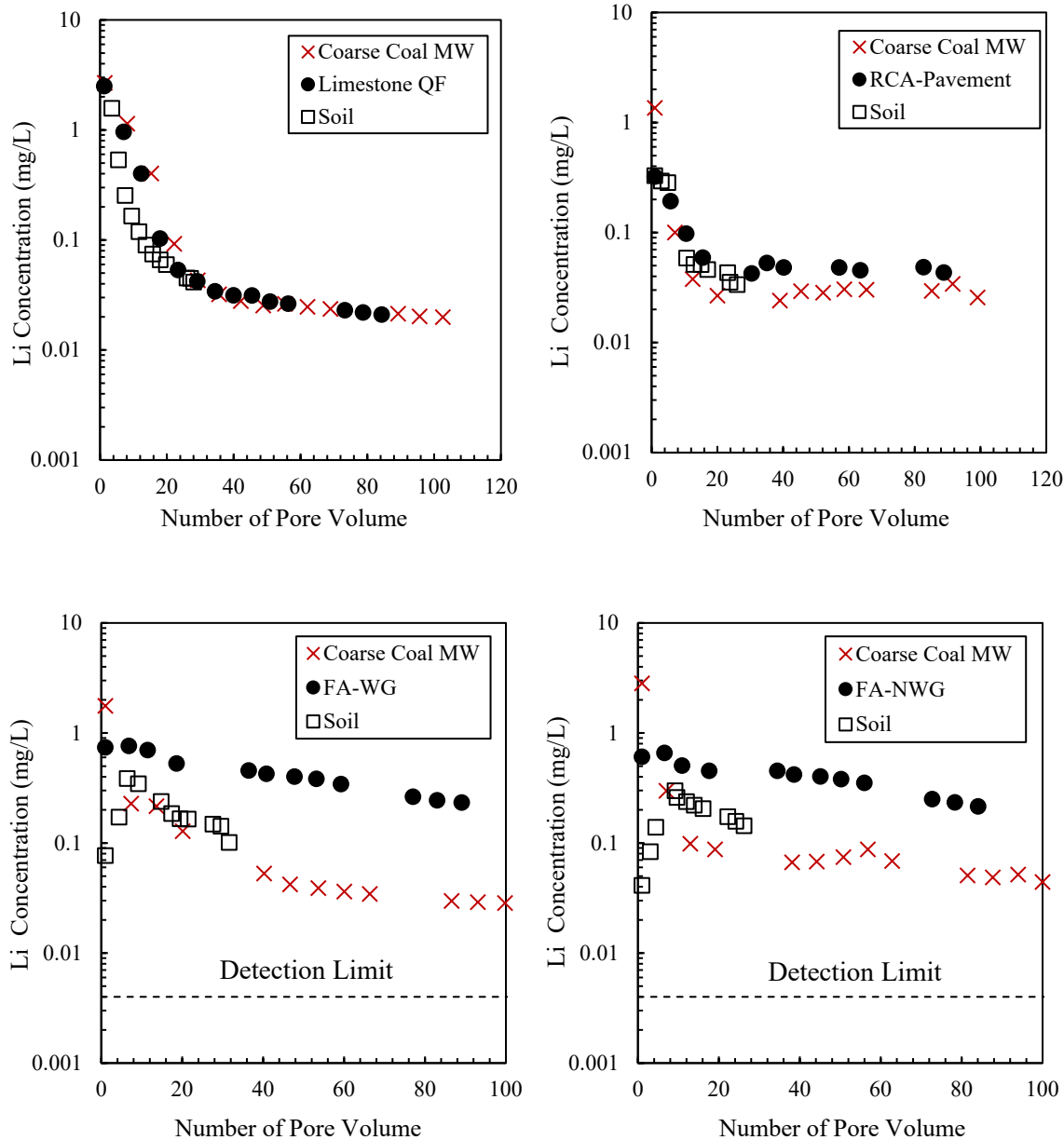


Figure 40. Li concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash. There is no MCL for Li.

As shown in Figure 41, initial Mo concentrations in the Sunrise coarse CMD were ~1 mg/L after which the concentrations decreased rapidly with increasing flow volume. Though stockpiled Sub-Bituminous fly ash treatment appeared to increase the Mo concentrations in the first pore volume, this treatment was the most effective method for Mo removal from this CMD.

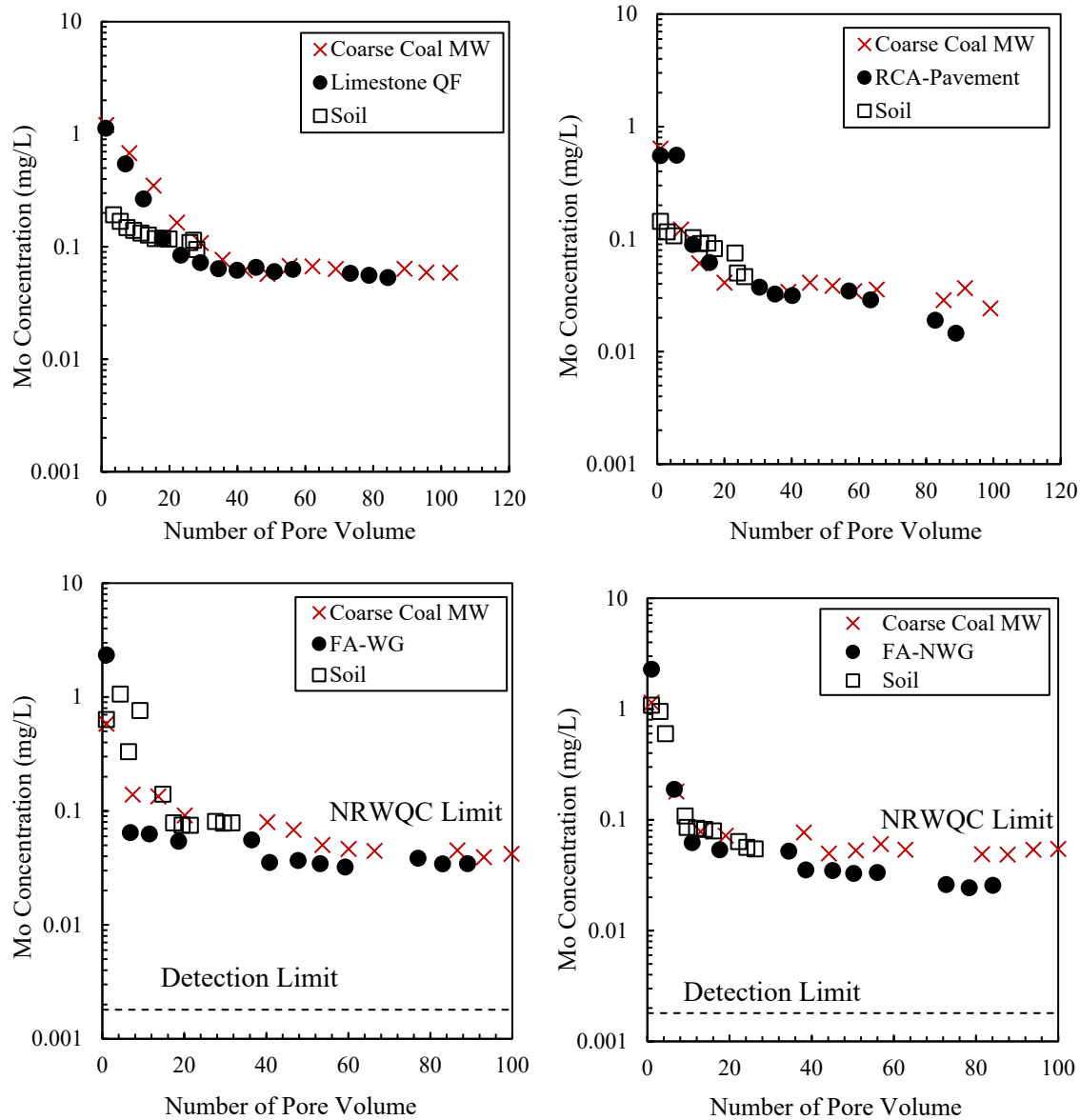


Figure 41. Mo concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, NRWQC = National Recommended Water Quality Criteria.

As shown in Figure 42, Ni concentrations in Sunrise coarse CMD started at ~10 mg/L and decreased to below MCL by 70 pore volumes. Similar to above metals, stockpiled Sub-Bituminous fly ash treatment was observed to be the most effective for Ni removal from this CMD.

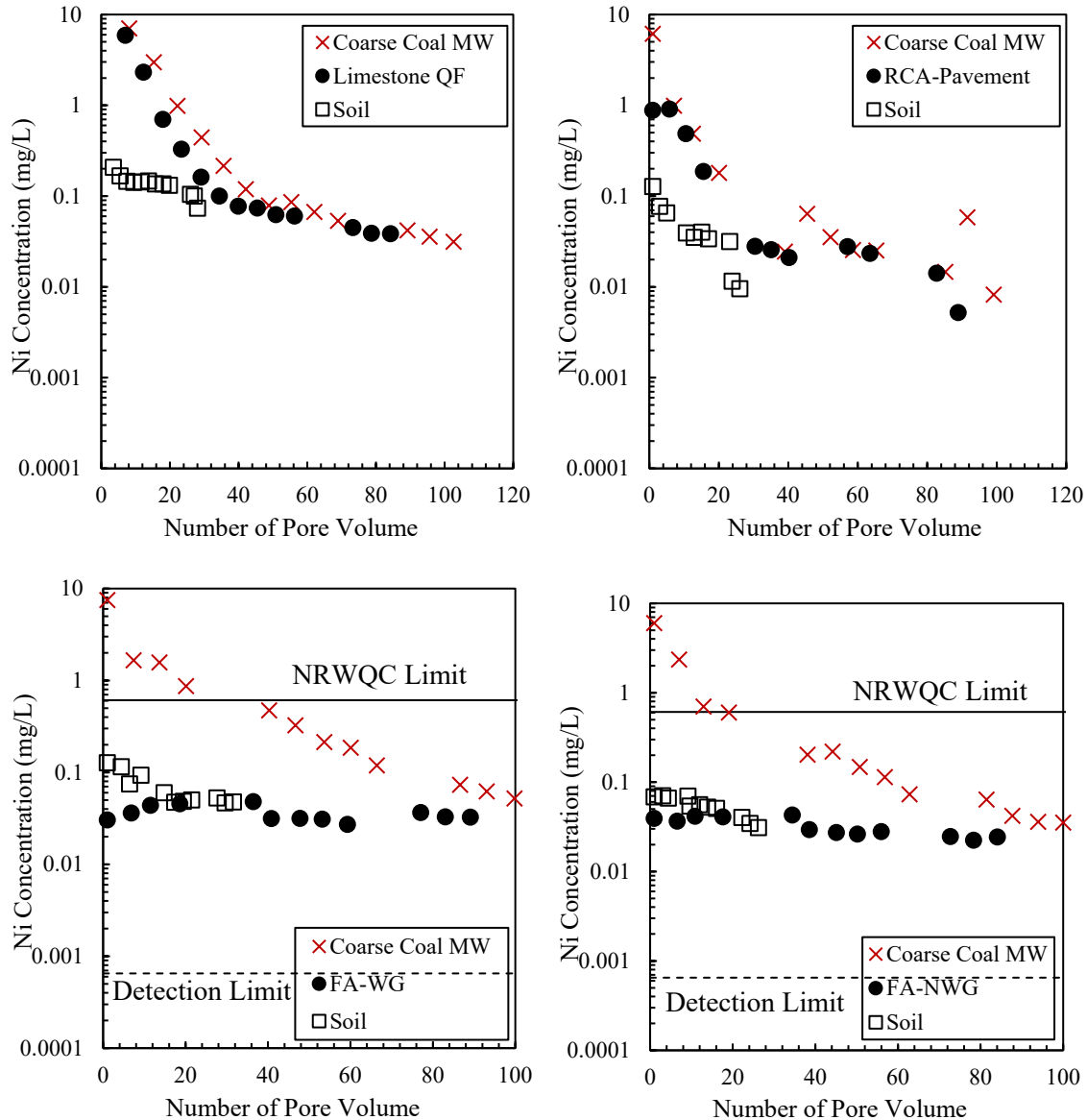


Figure 42. Ni concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, NRWQC = National Recommended Water Quality Criteria.

As shown in Figure 43, initial Pb concentrations in Sunrise coarse CMD were ~10 mg/L, after which the concentrations decreased until they plateaued between 0.1-0.3 mg/L. Though limestone quarry fines were also effective in removing Pb, stockpiled Sub-Bituminous fly ash treatment appeared to be the most suitable for Pb removal from this CMD. However, these treatments were only able to decrease Pb levels to ~0.1 mg/L.

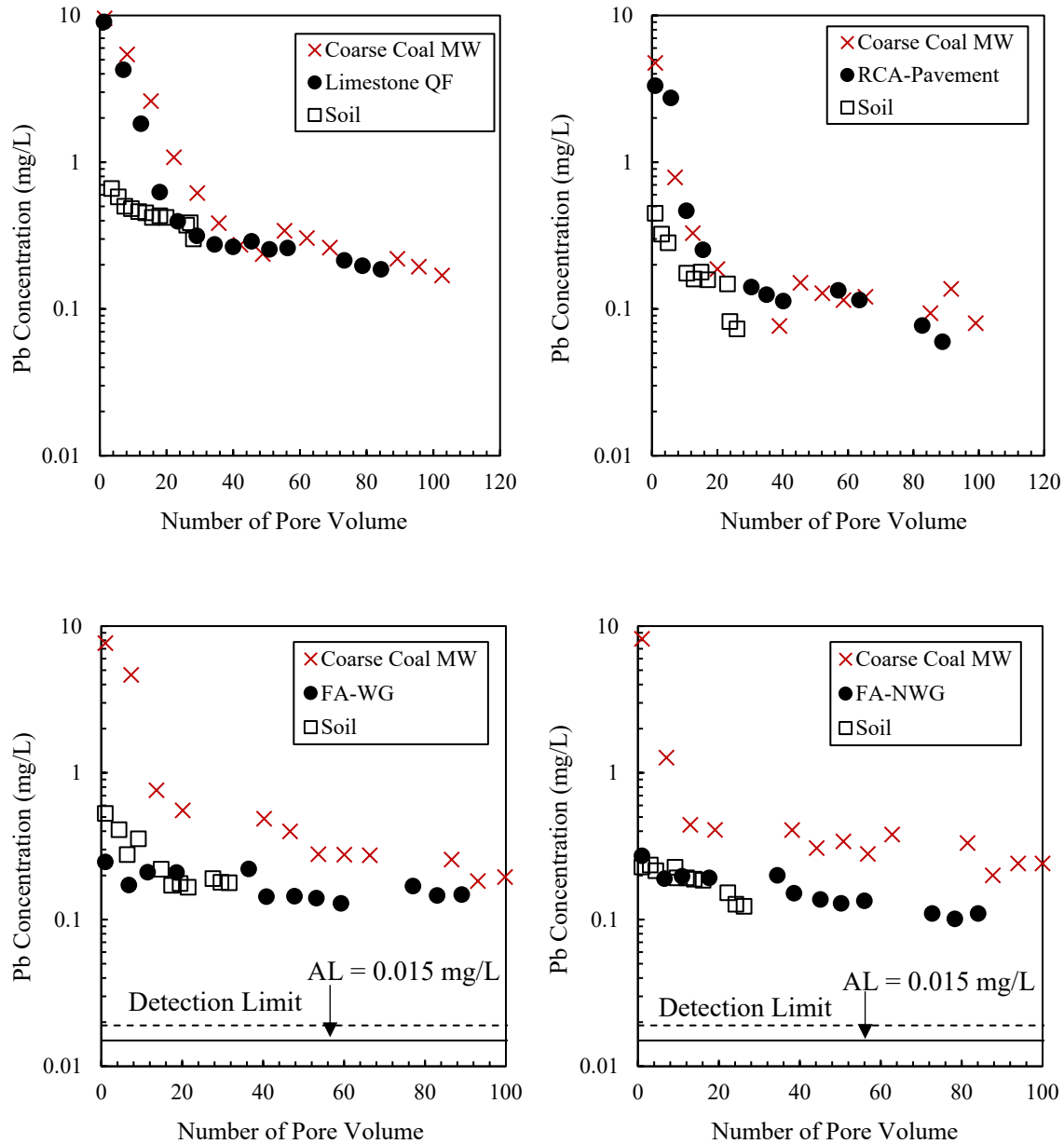


Figure 43. Pb concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, AL = Action Level.

As shown in Figure 44, Se concentrations ranged from ~10 mg/L to ~0.9 mg/L in the Sunrise coarse CMD in these CLTs. Though limestone quarry fines were able to decrease Se concentrations in initial pore volumes, stockpiled Sub-Bituminous fly ash treatment was the most effective in Se removal in this CMD. However, the Se concentrations even after successful treatment were above the MCL.

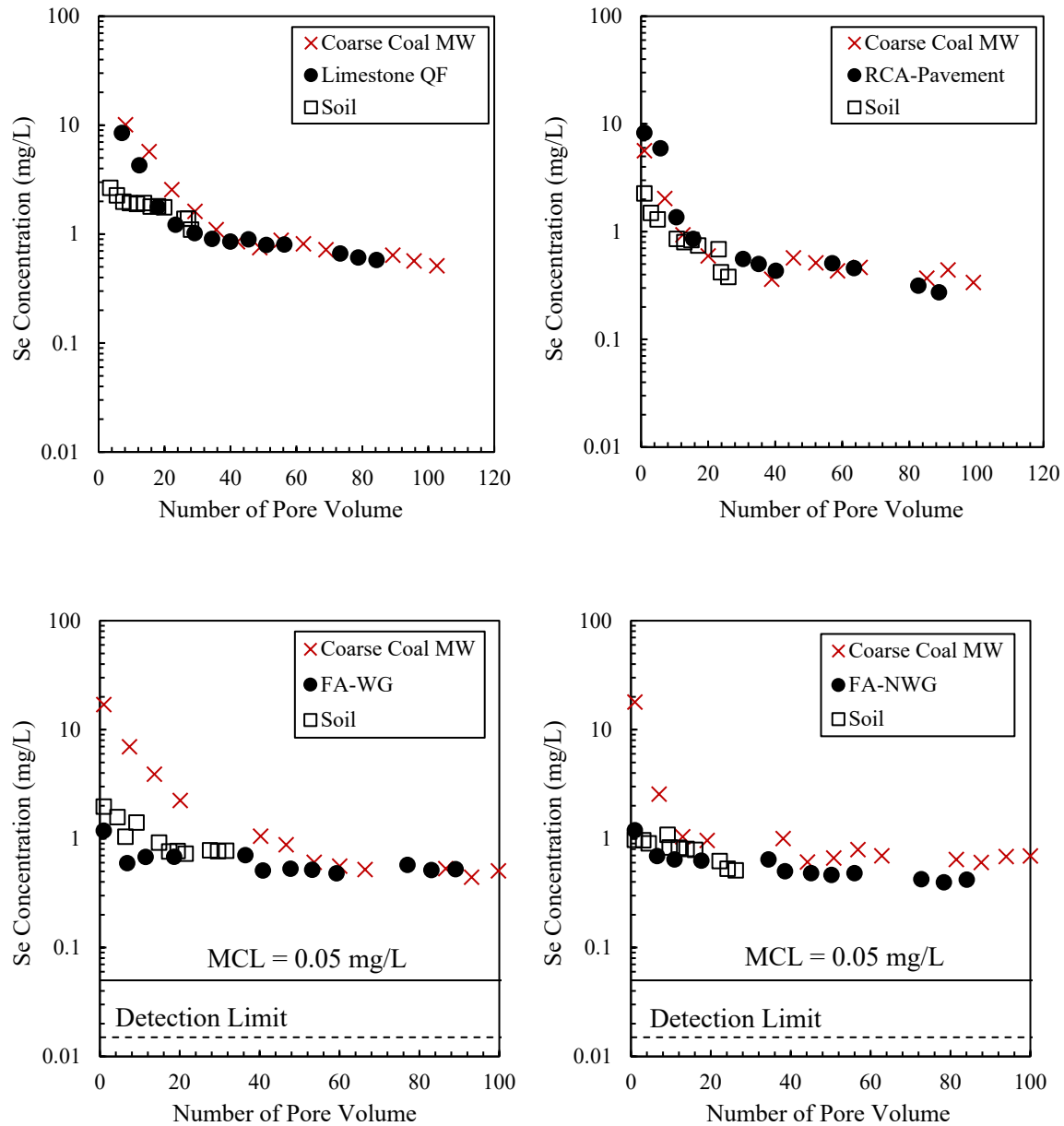


Figure 44. Se concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash, MCL = Maximum Contamination Level.

As shown in Figure 45, initial V concentrations in the Sunrise coarse CMD were ~1 mg/L, after which concentrations dropped to ~0.01 mg/L within 40 pore volumes. Overall, most of the industrial byproduct treatments appeared to be ineffective in removing V. In fact, fly ash treatment resulted in higher V concentrations compared to untreated CMD, suggesting that the fly ash leached V under these experimental conditions. Overall, compared to the other materials, limestone quarry fines seemed to be more effective in V removal from this CMD.

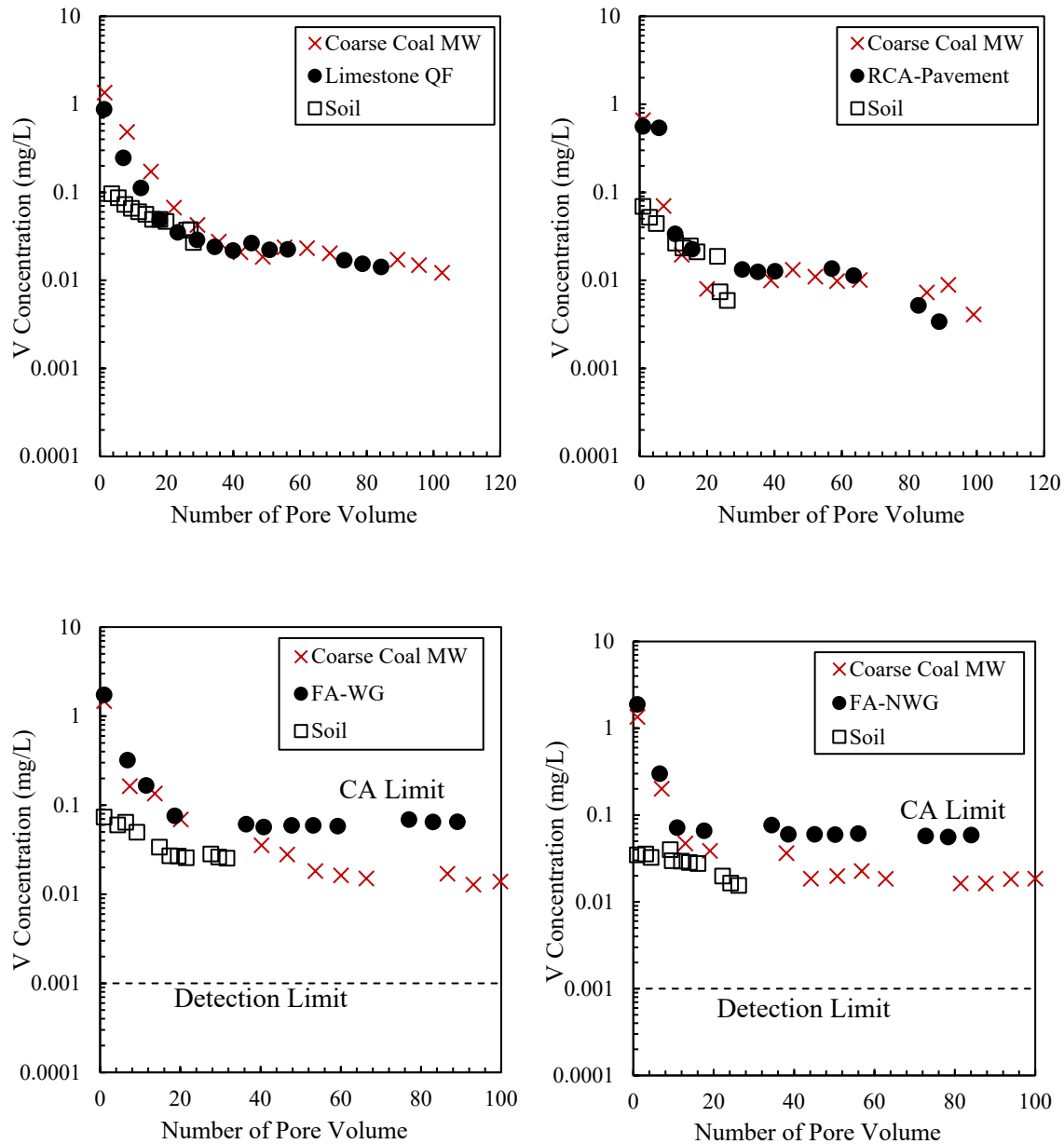


Figure 45. V concentrations for treatment of Bituminous coarse coal refuse from Sunrise Coal Mine, IN (Coarse Coal MW) with limestone quarry fines (Limestone QF), pavement RCA (RCA-Pavement), and stockpiled Sub-Bituminous fly ash using woven geotextile (WG), and non-woven geotextile (NWG). Note: FA = Fly Ash.

6. OBJECTIVE 3: Simulate water quality under variable field conditions

Geochemical modeling was performed using the data collected from the sequential batch WLTs in Objective 1 to determine the dominant oxidation states of the leached contaminants and their leaching control mechanisms.

The leaching of elements is controlled by two equilibrium mechanisms: solubility (dissolution and precipitation) and sorption. The geochemical equilibria models, based on thermodynamic data, have been proven effective in determining the equilibrium concentrations of the elements when the leaching mechanism was controlled by solubility. In this study, a numerical model, Visual MINTEQ, was used to identify the potential solubility controlling solids for each element. The metal concentrations leached from the materials at different pH conditions, along with the redox potential, sulfate concentrations, alkalinity, and dissolved organic and inorganic concentrations were considered as the input parameters. An equilibrium with atmosphere at 25°C was considered since the sample filtration procedure was performed in ambient conditions. For the redox-sensitive elements, their dominant oxidation states were considered for analyses. From geochemical modeling, the log activity of the elements as a function of effluent pH was determined. In addition, the saturation indices of the potential minerals controlling the leaching of the elements were determined.

6.1 Leaching mechanism of elements from mine wastes

The leaching of As from anthracite and Sub-Bituminous mine wastes was controlled by Ca-As solid solution, $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Figure 46). In contrast, As leaching from Bituminous mine wastes was regulated by $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$.

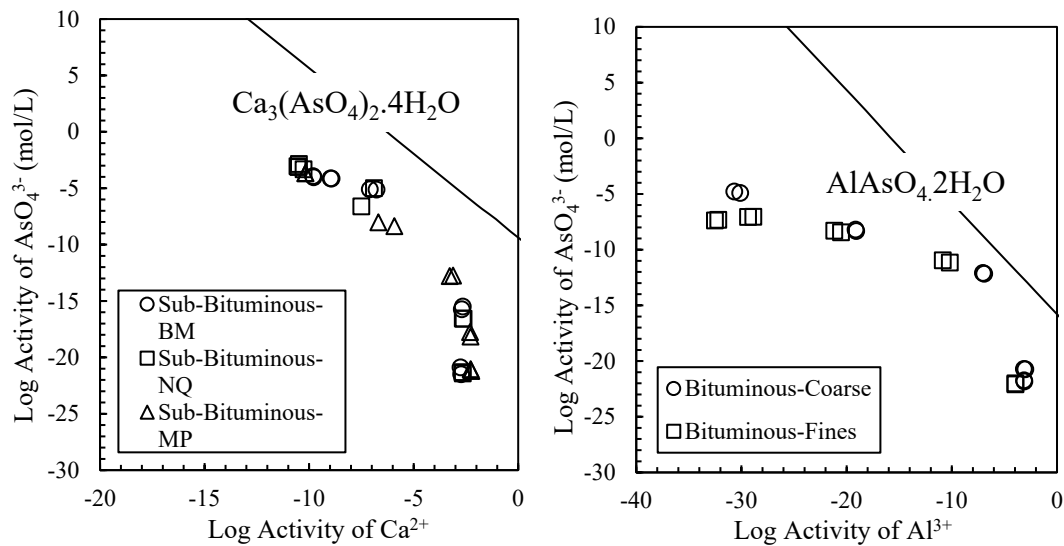


Figure 46. Log-activity diagram of As from Sub-Bituminous and Bituminous mine wastes.

Geochemical modeling indicated that $\text{Be}(\text{OH})_2$ controlled the leaching of Be from mine wastes at alkaline conditions (Figure 47). At acidic pH values, Be leaching from the mine wastes was sorption controlled.

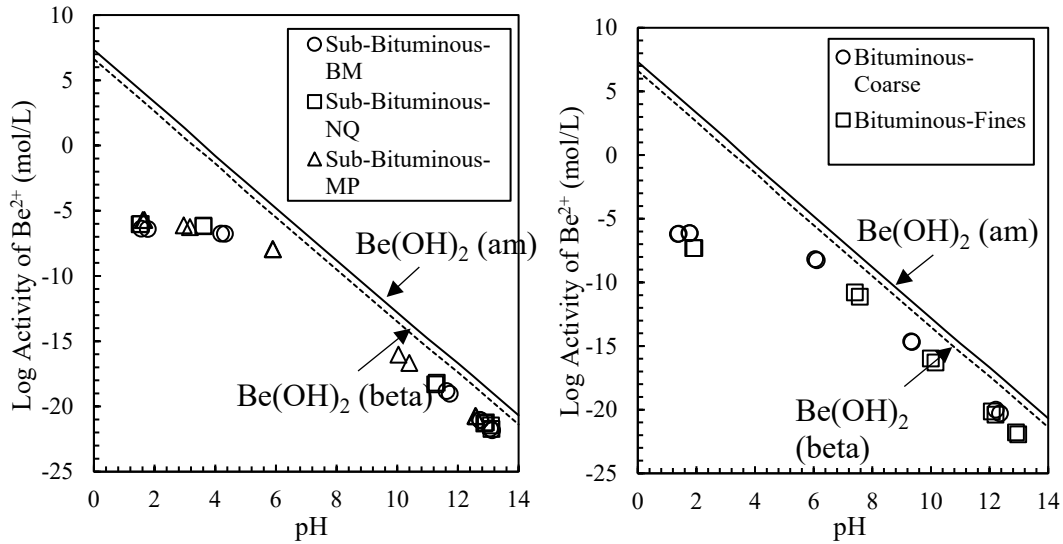


Figure 47. Log-activity diagram of Be from Sub-Bituminous and Bituminous mine wastes.

As shown in Figure 48, Cd leaching from mine wastes was governed by carbonate minerals, otavite, in basic pH conditions. At lower pH values, Cd leaching was solubility controlled. Slight oversaturation was observed for Bituminous mine wastes with respect to the otavite solubility line. This may have happened due to the presence of hydr(oxide) minerals of Cd. Cadmium hydroxide was also predicted by geochemical modeling.

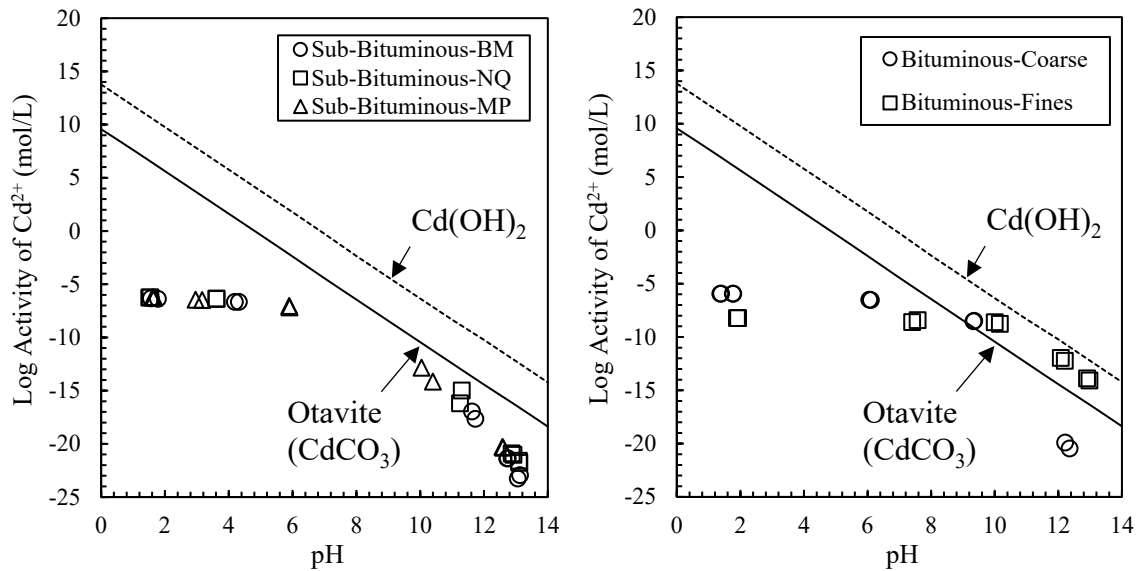


Figure 48. Log-activity diagram of Cd from Sub-Bituminous and Bituminous mine wastes

Figure 49 shows the log-activity diagram of Cr for mine wastes used in this study. Cr leaching was consistently governed by the solubility of Cr_2O_3 . $\text{Cr}(\text{OH})_3$ was also predicted by the geochemical modeling. As shown in Figures 50, tenorite was the major solubility controlling solid controlling

the release of Cu from the mine wastes. However, at pH values lower than 5, Cu leaching was controlled by sorption mechanism.

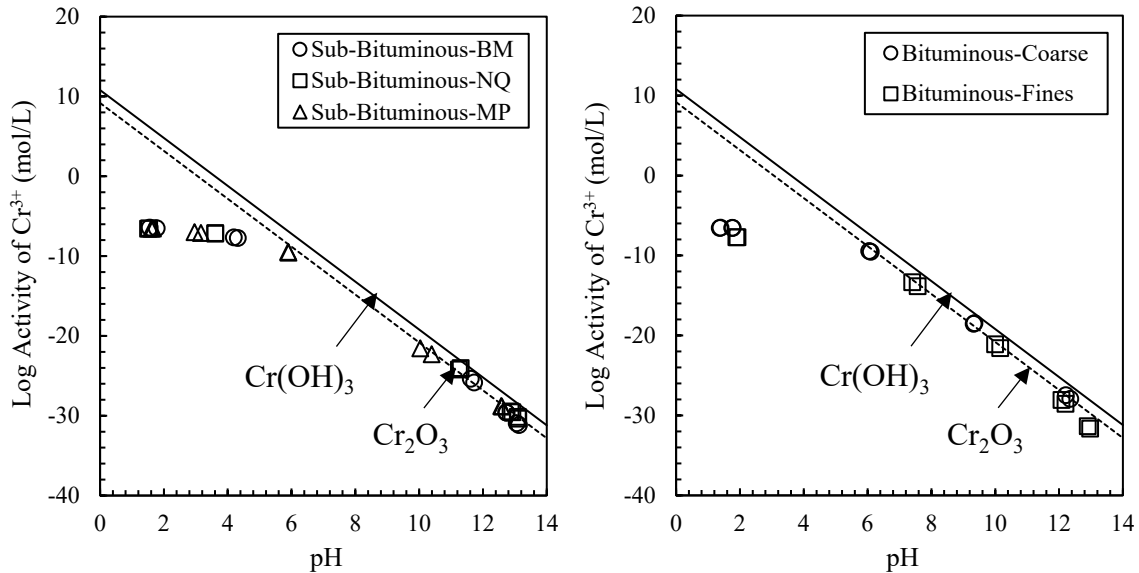


Figure 49. Log-activity diagram of Cr from Sub-Bituminous and Bituminous mine wastes.

Lithium molybdate (Li_2MoO_4) was the only solid controlling the effluent concentrations of Li in mine waste leachate (Figures 51). Geochemical modeling predicted only FeMoO_4 as the solid controlling the leaching of Mo from mine wastes (Figures 52).

Figures 53 revealed that between the pH values of 9 and 13, the leaching of Ni from mine wastes was controlled by NiCO_3 . At pH values lower than 9, morenosite ($\text{NiSO}_4 \cdot 7(\text{H}_2\text{O})$) was the solubility controlling solid for Ni. Slight oversaturation with respect to the solubility of NiCO_3 was observed for Sub-Bituminous and Bituminous mine wastes due to the presence of nickel hydr(oxide) minerals. Figures 54 showed that Pb leaching was controlled by anglesite at lower pH values (under 6) and $\text{Pb}(\text{OH})_2$ above pH 6.

Figure 56 shows that the leaching of Se from the mine wastes was controlled by $\text{CaSeO}_3 \cdot 2\text{H}_2\text{O}$ and quartz, respectively. The geochemical modeling predicted no other minerals of Se. The geochemical modeling only predicted $\text{Fe}(\text{VO}_3)_2$ as the solubility controlling solid controlling the leaching of V from mine wastes (Figures 57).

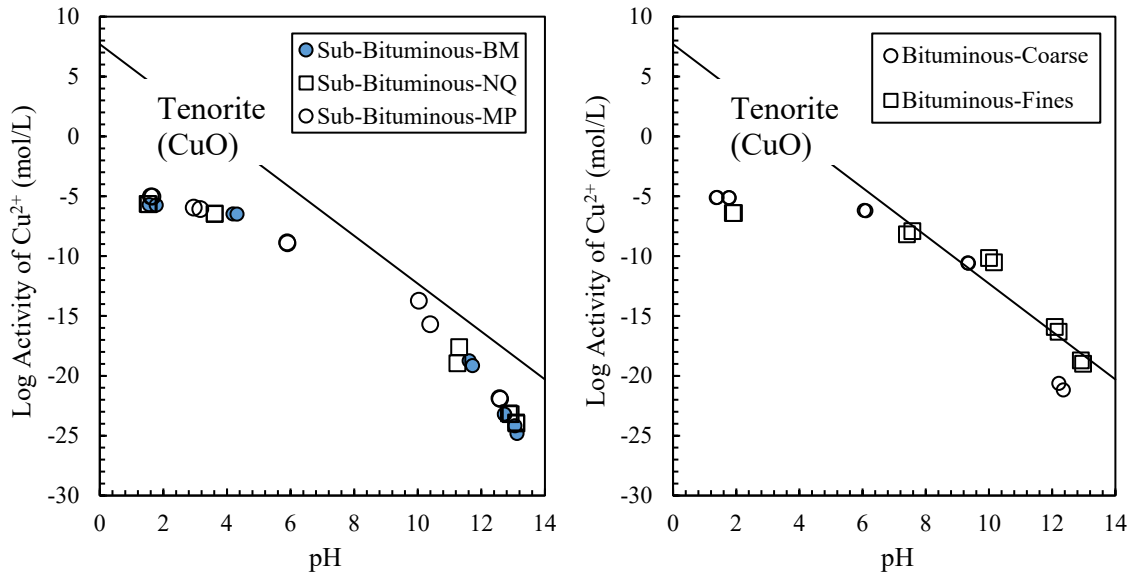


Figure 50. Log-activity diagram of Cu from Sub-Bituminous and Bituminous mine wastes

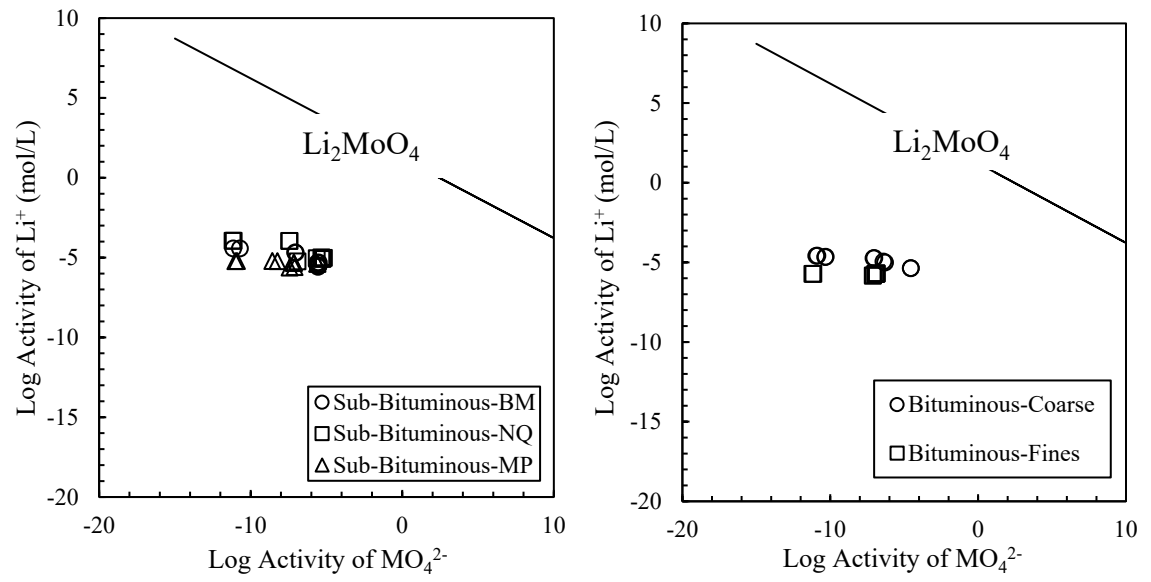


Figure 51. Log-activity diagram of Li from Sub-Bituminous and Bituminous mine wastes

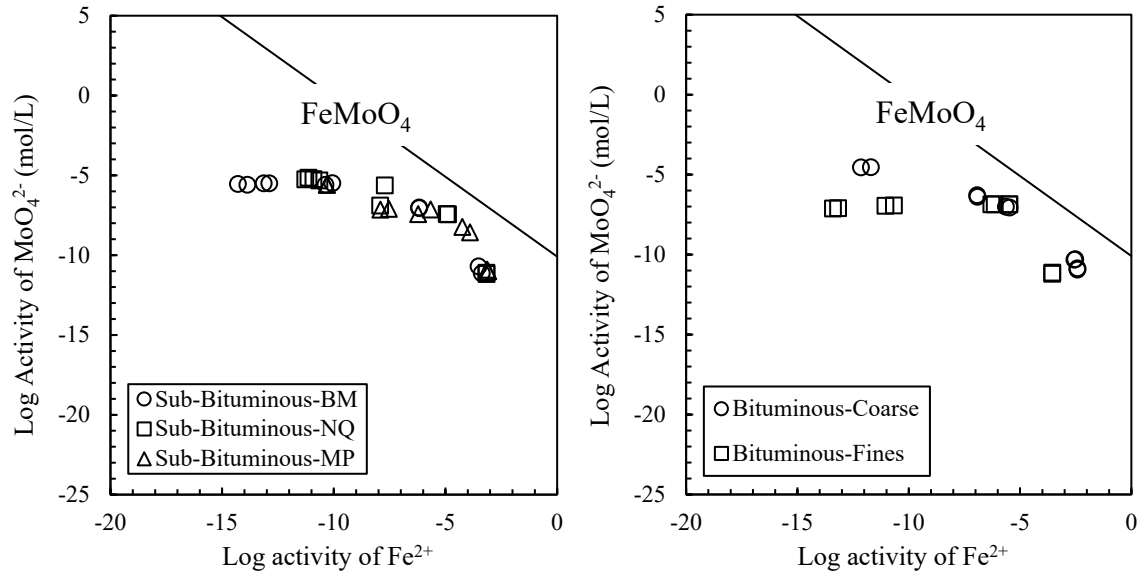


Figure 52. Log-activity diagram of Mo from Sub-Bituminous and Bituminous mine wastes

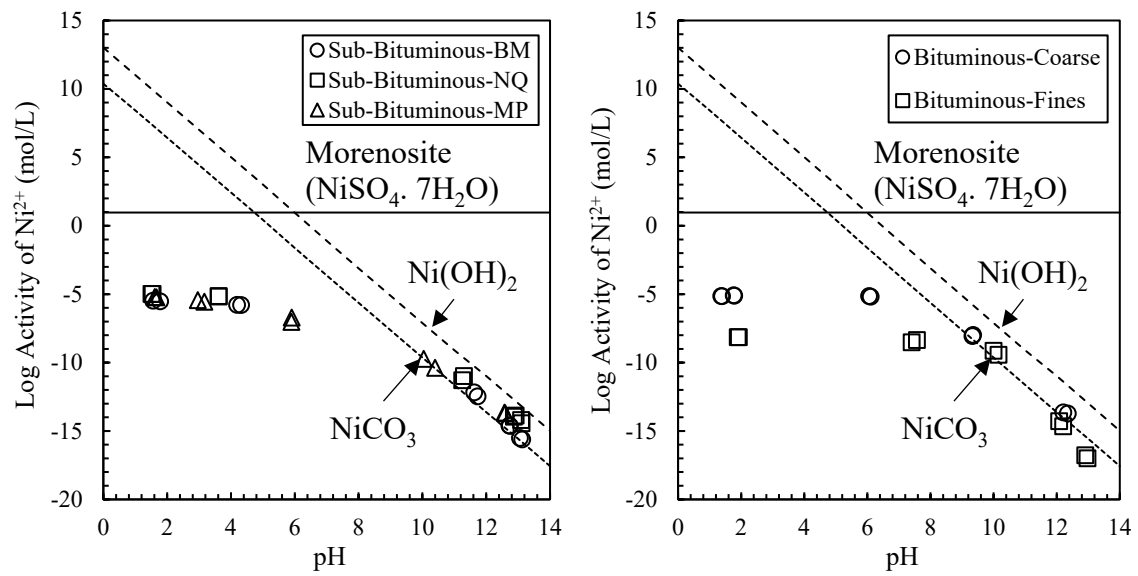


Figure 53. Log-activity diagram of Ni from Sub-Bituminous and Bituminous mine wastes

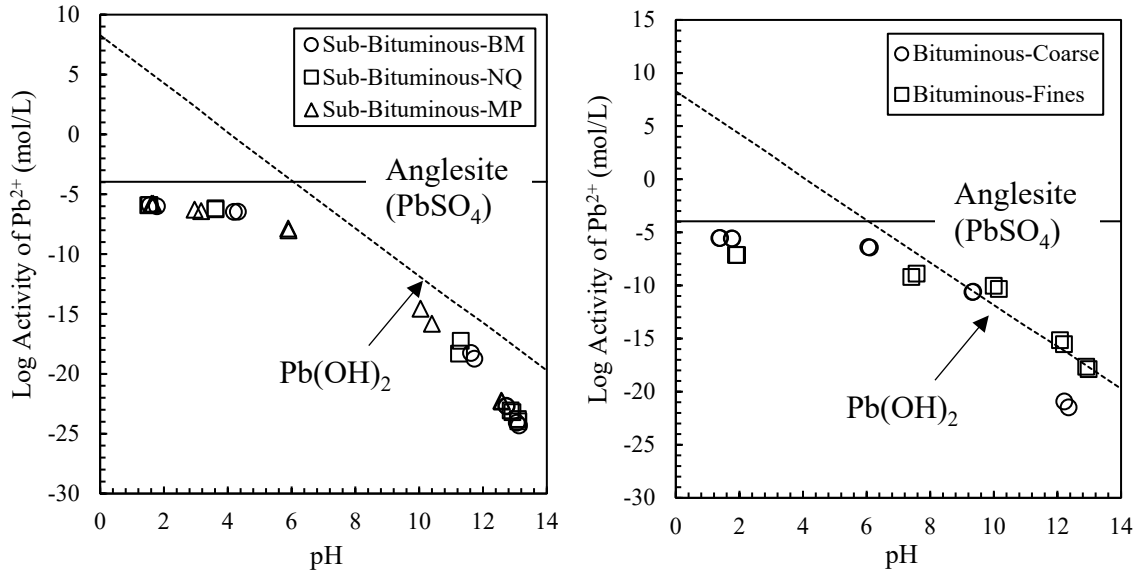


Figure 54. Log-activity diagram of Pb from Sub-Bituminous and Bituminous mine wastes

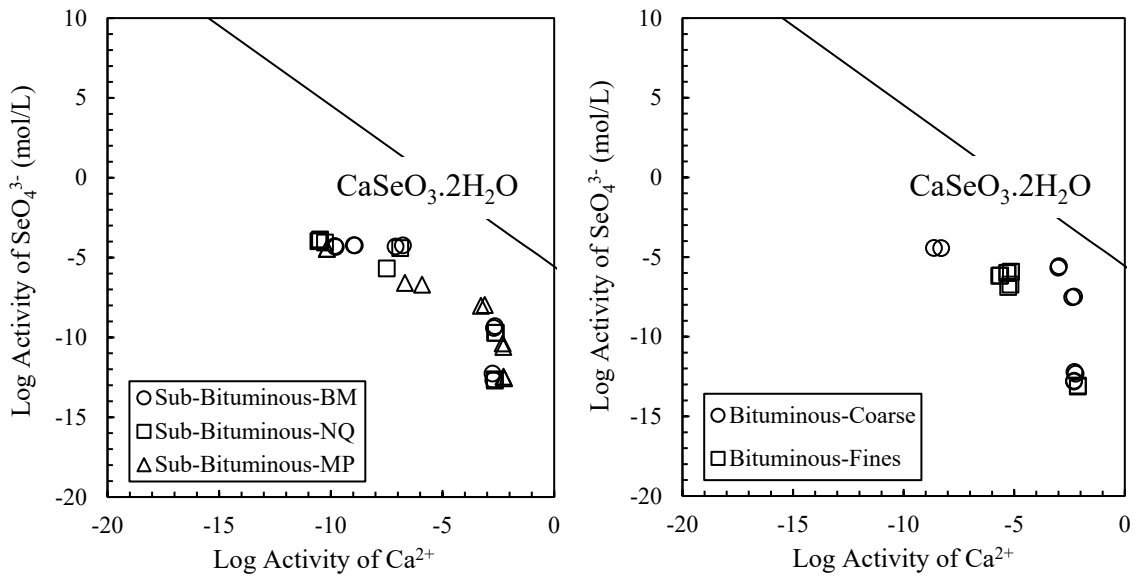


Figure 55. Log-activity diagram of Se from Sub-Bituminous and Bituminous mine wastes

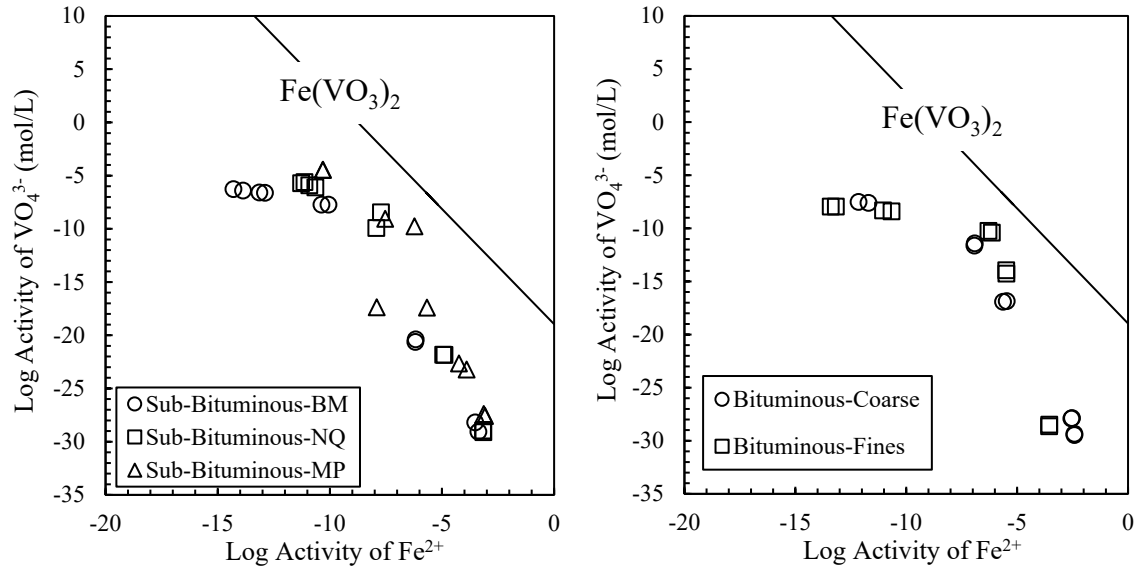


Figure 56. Log-activity diagram of V from Sub-Bituminous and Bituminous mine wastes.

6.2 Leaching Mechanism of elements from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA)

Figure 57 shows the log activity-pH diagram of As leached from RCA, quarry fines, and fly ash used in this study. As leaching from RCA was controlled by the solubility of $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$. On the other hand, $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ was the solubility controlling solid for quarry fines. Conversely, $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ maintained the leaching of As from fly ash.

Between the pH of 5 and 13, Be leaching from RCA, quarry fines, and fly ash was governed by $\text{Be}(\text{OH})_2$ (Figures 58). At pH values lower than 5, Be leaching was sorption controlled.

Figures 59 show that in the pH range of 8 to 13, Cd leaching from RCA, quarry fines, and fly ash was regulated by otavite. At acidic conditions, Cd leaching was solubility controlled. Again for the fly ash, oversaturation with respect to otavite was observed due to the presence of $\text{Cd}(\text{OH})_2$.

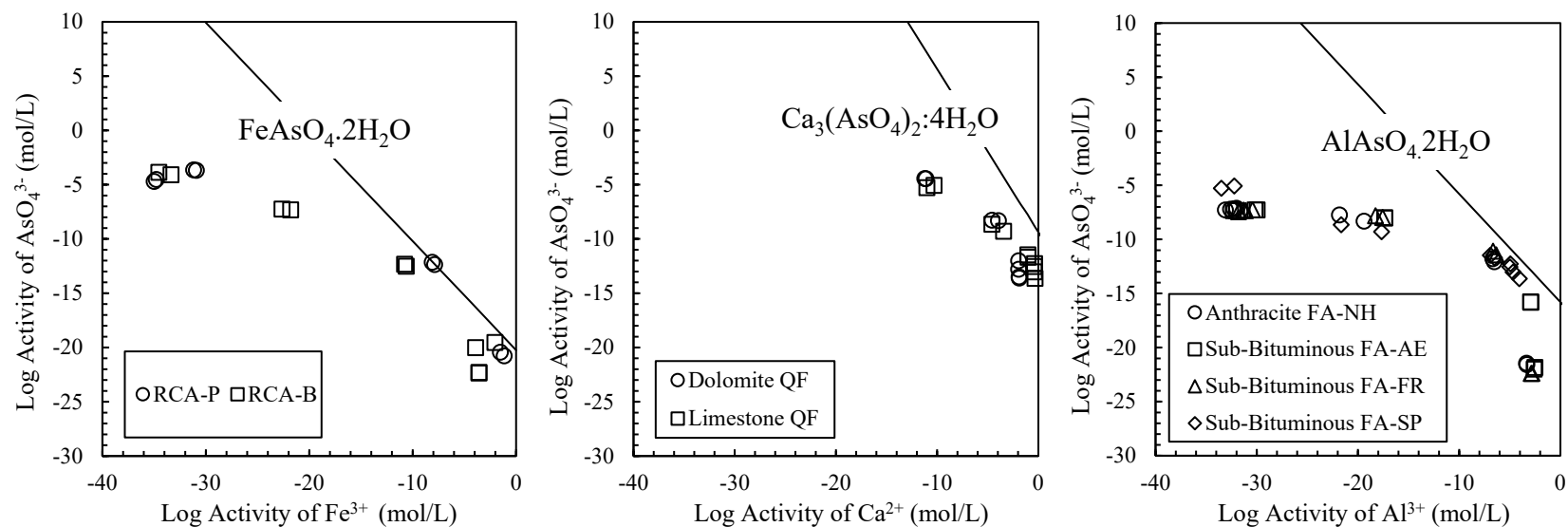


Figure 57. Log-activity diagram of As from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA)

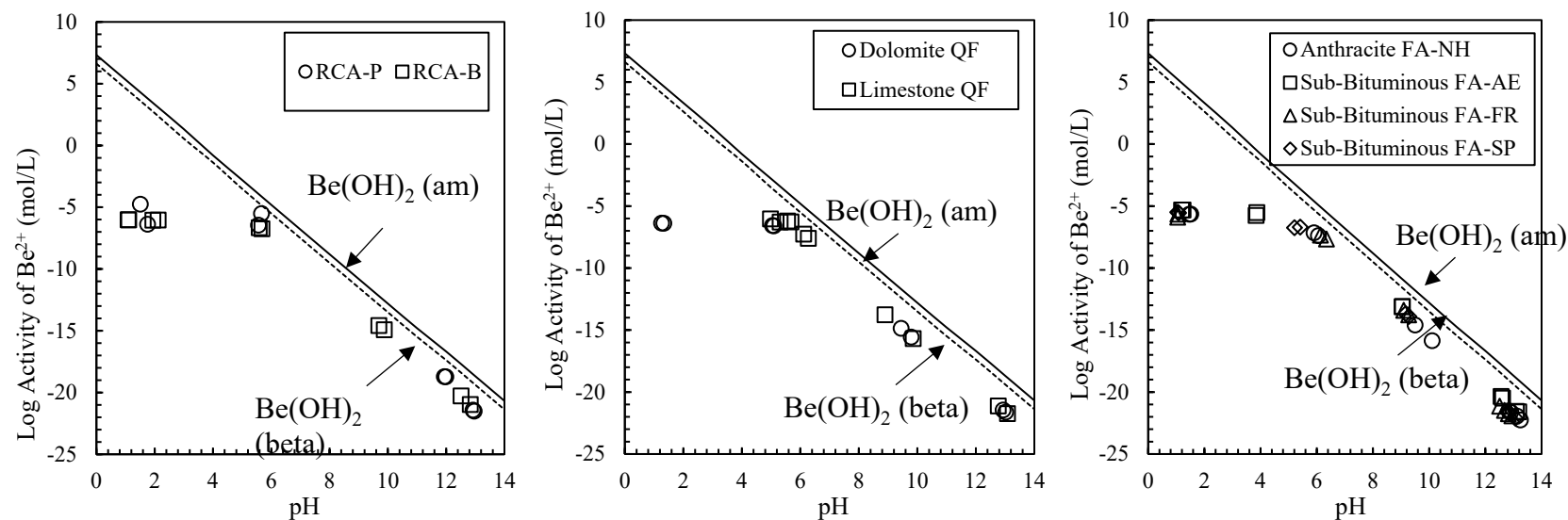


Figure 58. Log-activity diagram of Be from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA)

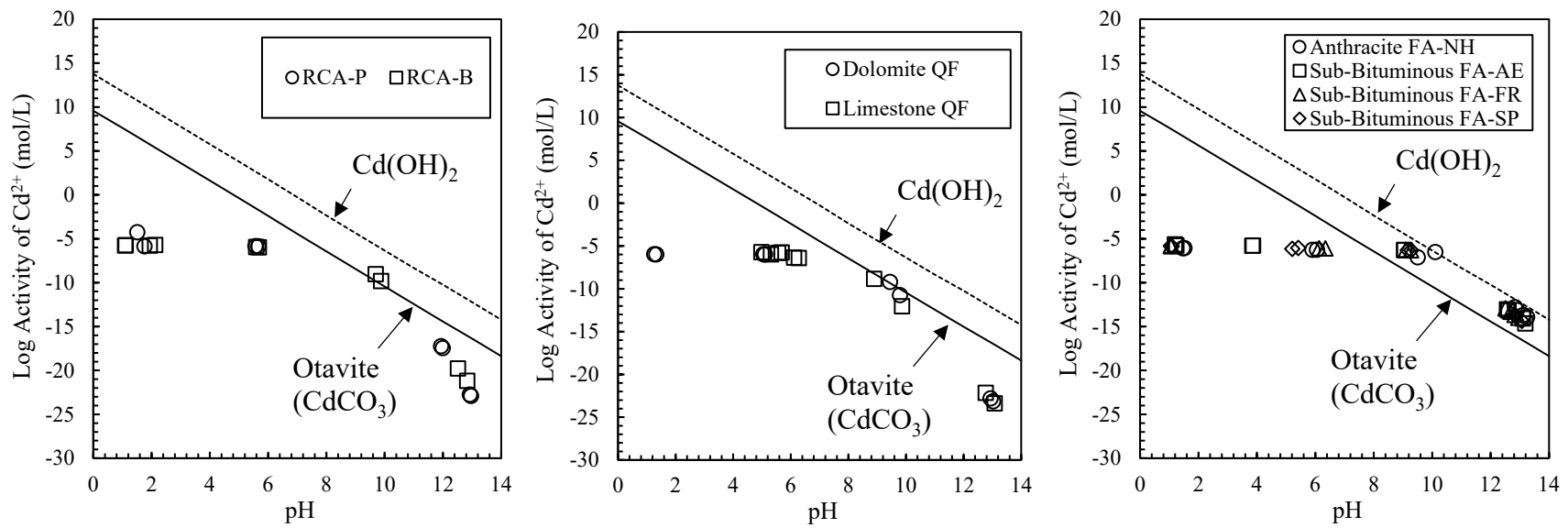


Figure 59. Log-activity diagram of As from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA)

As shown in Figure 60, Cr leaching from RCA, quarry fines, and fly ash was either regulated by Cr_2O_3 or $\text{Cr}(\text{OH})_3$ between the pH of 5 and 13. At pH values lower than 5, the leaching of Cr from the treatment materials was sorption controlled.

Figures 61 show that the leaching of Cu from the treatment materials was controlled by tenorite between the pH values of 6 and 13. At pH lower than 6, Cu leaching was sorption controlled. For the fly ash, slight oversaturation with respect to tenorite solubility was observed.

For Li, Li_2MoO_4 was predicted to be the solubility controlling solid for Li (Figure 62). For fly ash, with an increase in MoO_4^{2-} activity, Li activity decreased. Figure 63 show that MgMoO_4 was the solid controlling the leaching of Mo from RCA and quarry fines. In contrast, CaMoO_4 controlled Mo leaching from fly ash.

As depicted in Figure 64, Ni leaching from the treatment materials between the pH values of 2 and 7 could be controlled by morenosite. At pH higher than 8, the discharge of Ni from quarry fines was dominated by nickel carbonate. In contrast, the leaching of Ni from RCA and fly ash at pH values higher than 8 was governed by nickel hydroxide.

As shown in Figures 64(d), (e), and (f), the leaching of Pb from the treatment materials was controlled by anglesite when the effluent pH was between 2 and 6. At pH higher than 6, $\text{Pb}(\text{OH})_2$ controlled the leaching of Pb from RCA, quarry fines, and fly ash. Slight oversaturation with respect to $\text{Pb}(\text{OH})_2$ was observed, which may have happened due to the presence of Pb-sulfate mineral, anglesite.

Figures 65 show the Se leaching from RCA and quarry fines was regulated by $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$. Conversely, the release of Se from fly ash was dominated by $\text{CaSeO}_3 \cdot 2\text{H}_2\text{O}$. As illustrated in Figure 66, V leaching from RCA and quarry fines was controlled by Na_3VO_4 . In the case of fly ash, the leaching of V was dominated by $\text{Ca}_3(\text{VO}_4)_2$.

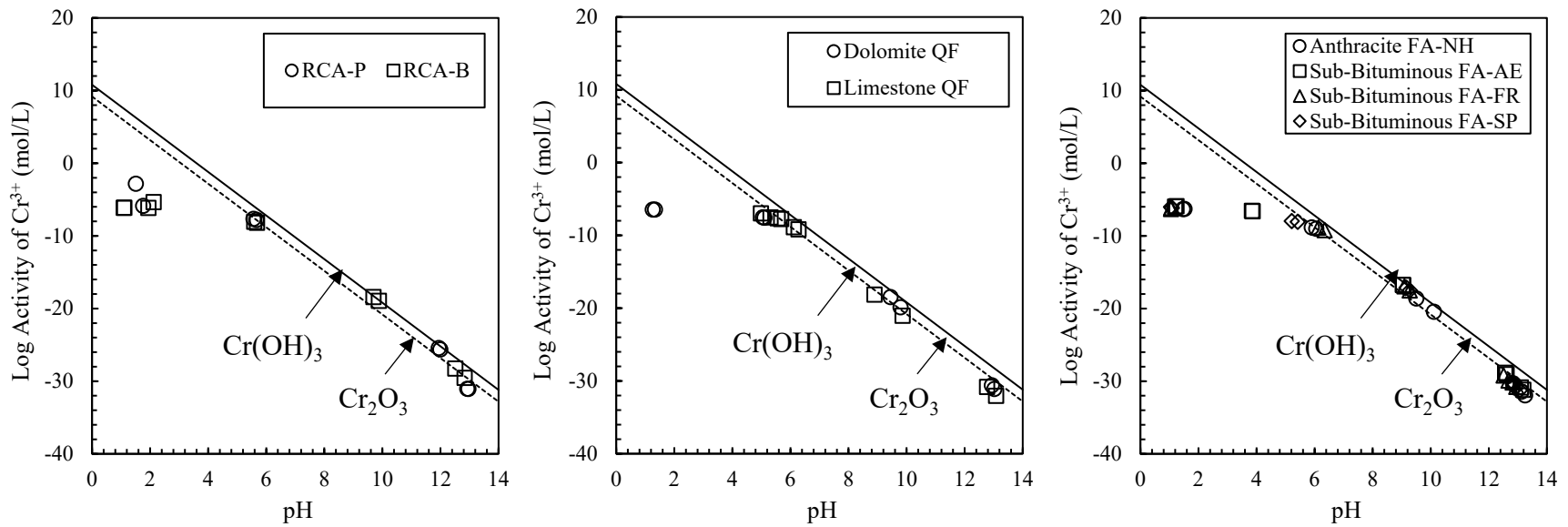


Figure 60. Log-activity diagram of Cr from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA)

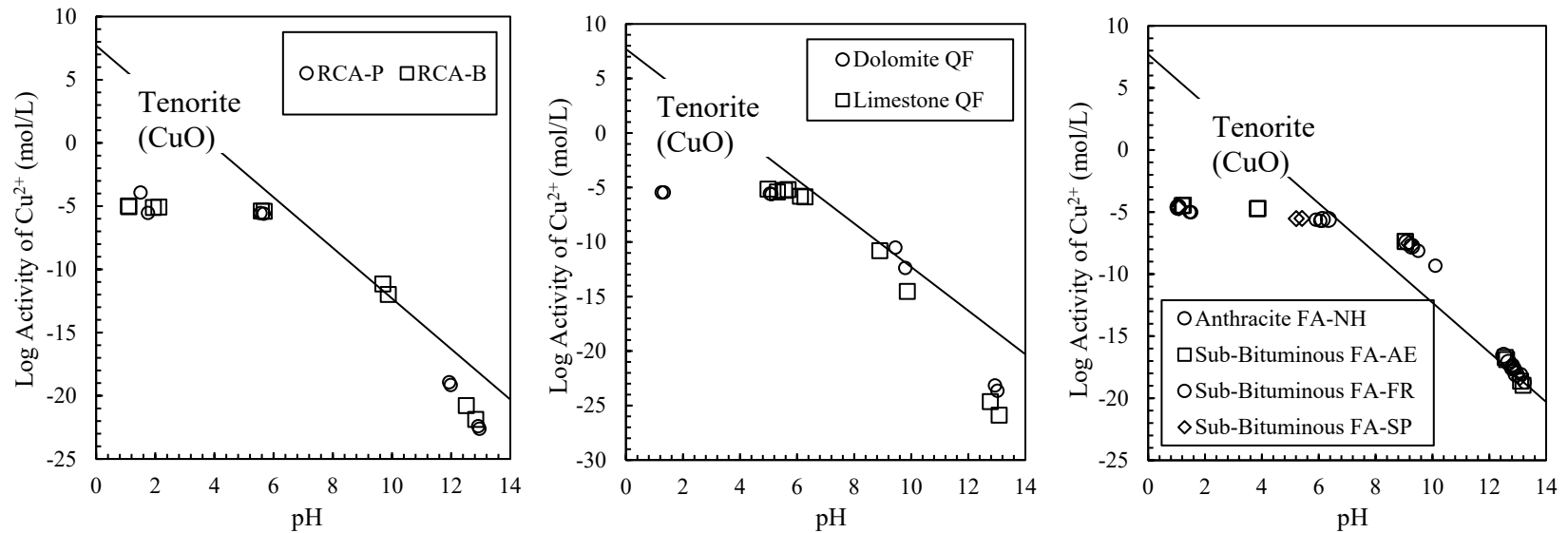


Figure 61. Log-activity diagram of Cu from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA)

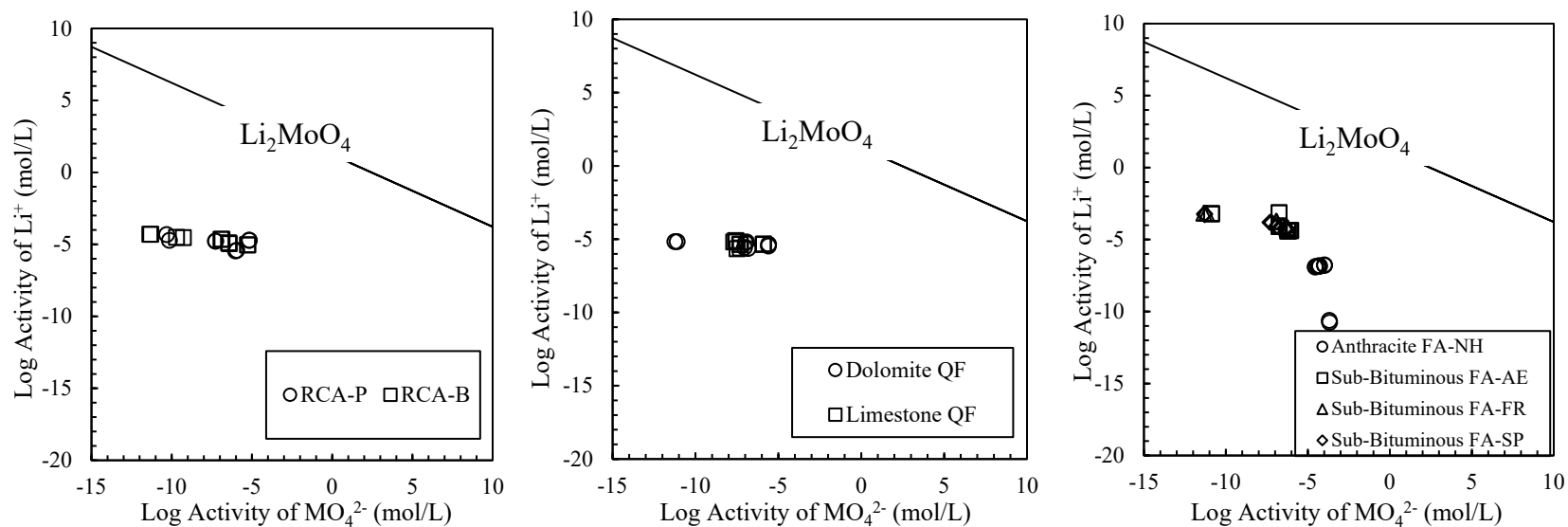


Figure 62. Log-activity diagram of Li from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA)

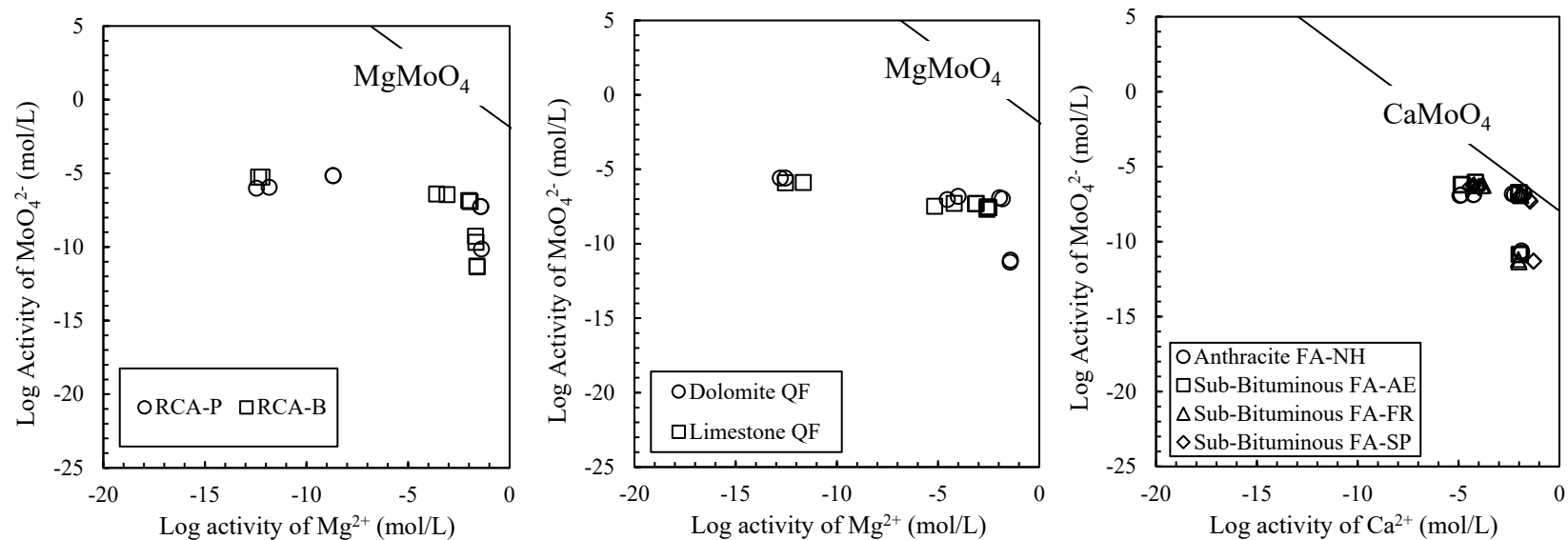


Figure 63. Log-activity diagram of Mo from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA)

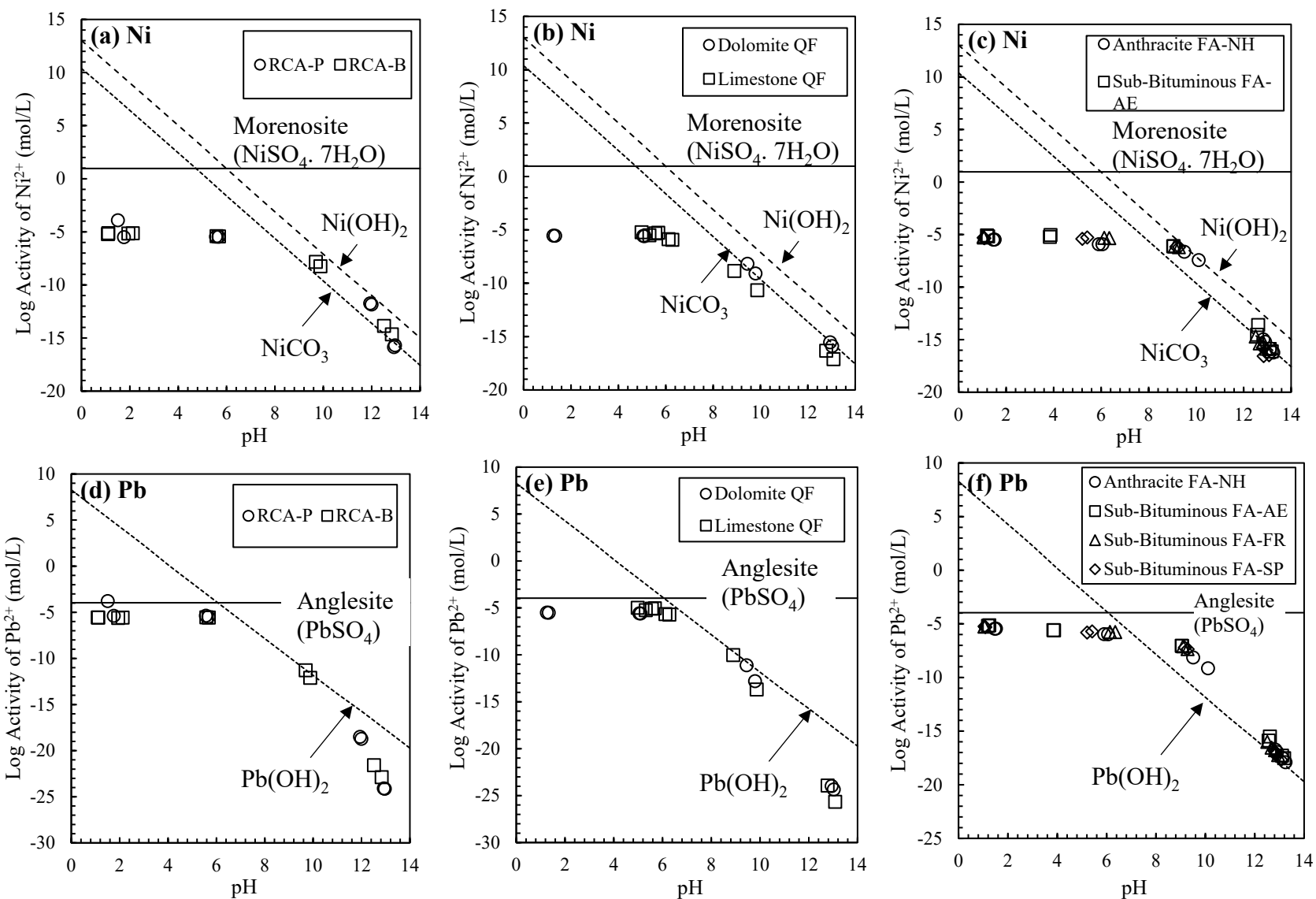


Figure 64. Log-activity diagram of Ni (a-c) and Pb (d-f) from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA)

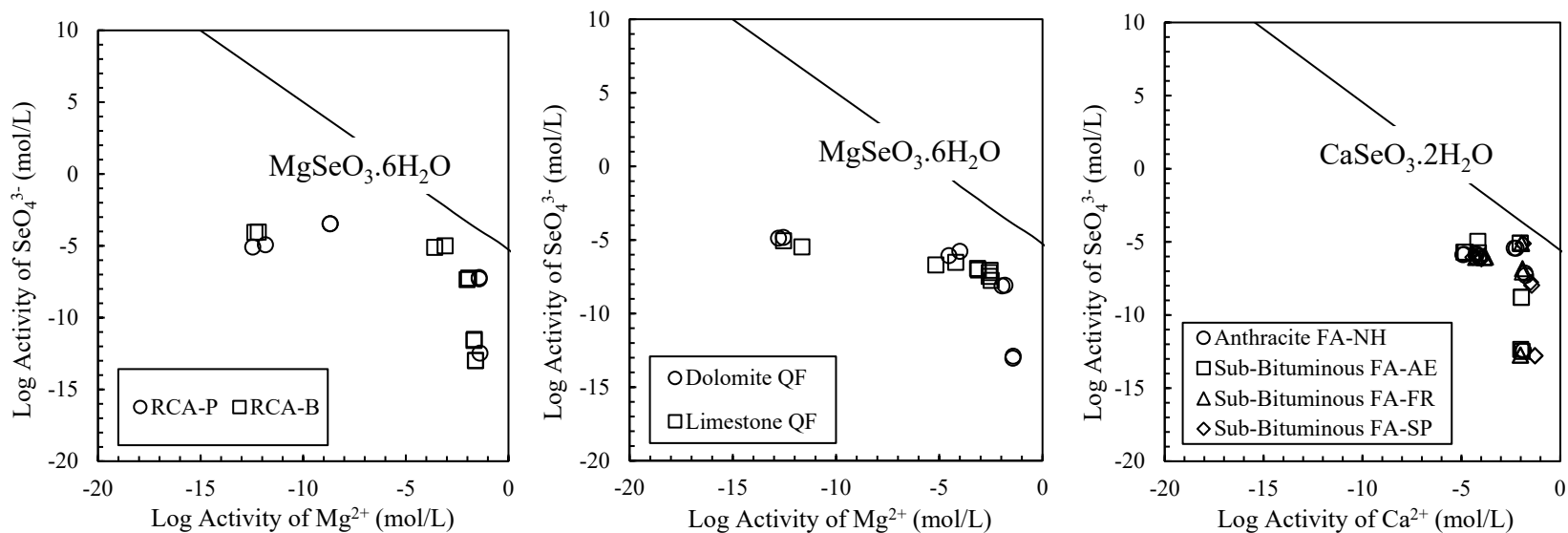


Figure 65. Log-activity diagram of Se from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA).

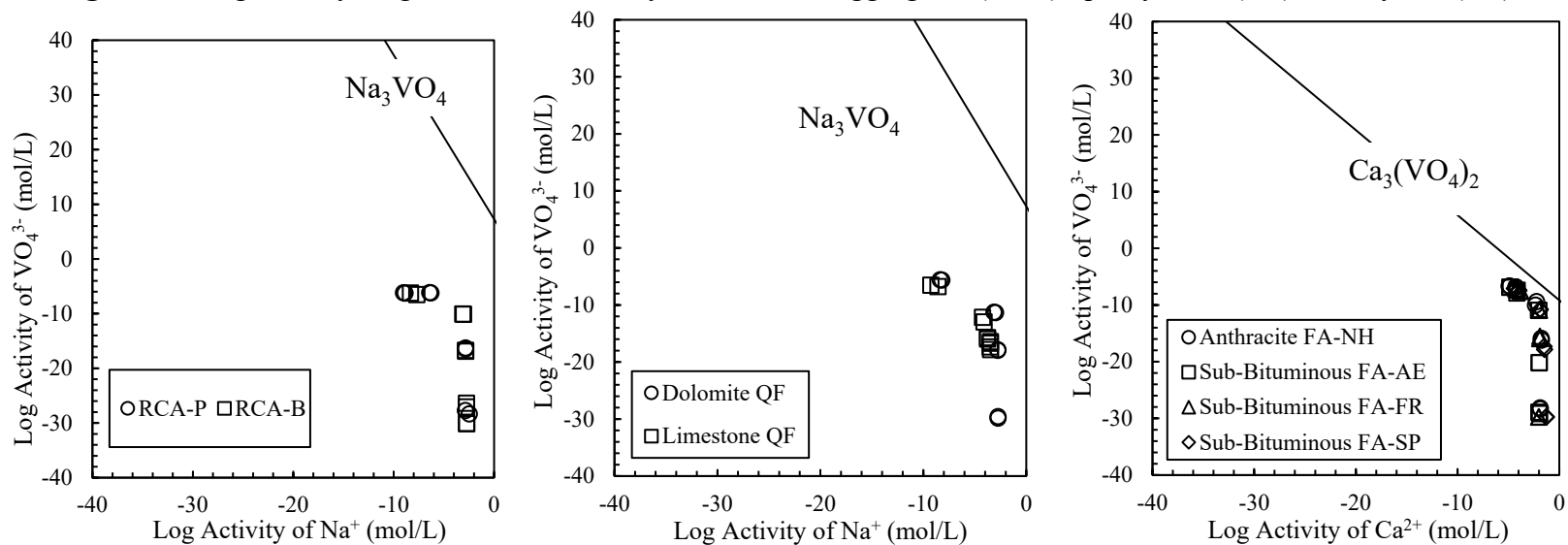


Figure 66. Log-activity diagram of V from recycled concrete aggregates (RCA), quarry fines (QF), and fly ash (FA).

7. OBJECTIVE 4: Evaluate the cost effectiveness of the use of industrial byproducts

As discussed above, limestone quarry, RCA from pavement waste, and Sub-Bituminous fly ash (stockpiled from Muscatine, IA) showed the highest potential to remediate CMD in the sequential batch WLTs (Objective 1). For this reason, life cycle analysis (LCA) and life cycle cost analysis (LCCA) were performed for CMD treatments considering only these industrial byproducts. The materials chosen for LCA and LCCA are the same as used in the sequential CLTs in Objective 2. For coal wastes, Sub-Bituminous coal refuse from Newquist, IA and Bituminous coarse coal refuse from Indiana were selected for CLTs due to their higher leaching potentials of heavy and trace metals. For the industrial byproducts for CMD treatment, one material from each type (fly ash, quarry fines, and RCAs) were chosen. Specifically, stockpiled Sub-Bituminous fly ash, limestone quarry fines, and RCA from pavement demolition waste were selected because these materials were the most efficient in removing certain metals (with focus on As, Be, Cd, Pb, and Se because those metals were present in relatively high concentrations in the CMD samples) from CMD in addition to effectively increasing the leachate pH and decreasing the sulfate concentrations.

7.1 Life cycle analysis (LCA)

LCA is a comprehensive approach to evaluate the environmental impacts and resources used by a product or process considering all stages in its life cycle. LCA is particularly useful because it allows for the consideration of environmental impacts transferred from one medium to another; this includes for example accounting for the leaching of contaminants from the industrial byproducts used in this study. The ISO framework for the life cycle assessment includes the definition of goal/purpose of the analysis, and the definition of the functional unit and system boundaries. The functional unit is a reference measure to which each input and output is related. The system boundaries define which unit processes will be included in the LCA study.

The LCA performed in this study aims to compare the impacts to the environment and human health by each industrial byproduct using a functional unit of 1 m³ of untreated CMD. The unit processes considered were the leaching of contaminants from each industrial byproduct and the remediation of the untreated CMD. The environmental footprint related to transportation and sludge disposal were not considered, therefore emissions to air and soil were not assessed, and only emissions to surface water were considered. Though it is possible that treated CMD could enter either surface water or groundwater depending on the treatment setup, surface water impacts are likely to be more direct and immediate compared to groundwater. Therefore, we focused the LCA on surface water to assess possible worst-case scenarios. Each CMD treatment was compared based on their impact in four impact categories: ecotoxicity, eutrophication, human-health carcinogenics and human-health non-carcinogenics. A brief description of each impact category is shown in Table 9.

Table 9. Description of impact categories considered (Acero et al., 2015).

	ECOTOXICITY	EUTHROPHICATION	HUMAN TOXICITY
Definition	Toxic effects of chemicals on an ecosystem	Accumulation of nutrients in aquatic systems	Toxic effects of chemicals on humans
Impact indicator	Biodiversity loss and/or extinction of species	<ul style="list-style-type: none"> • Increase of nitrogen and phosphorus concentrations • Formation of biomass (e.g. algae) 	Cancer, respiratory diseases, other non-carcinogenic effects and effects to ionizing radiation
Considerations	<ul style="list-style-type: none"> • Toxicological responses of different species • Nature of the chemicals in the ecosystem 	Transportation of the nutrients (air, water, wash-off from land)	<ul style="list-style-type: none"> • Toxicological responses of humans • Nature of the chemicals in the human body

In order to calculate the effect of each proposed treatment in the impact categories described above, we utilized two methods built in the OpenLCA software: (i) the TRACI method, which stands for the Tool for the Reduction and Assessment of Chemical and other environmental Impacts developed by the EPA using input parameters consistent with U.S. locations, and (ii) the ILCD method which stands for International Reference Life Cycle Data System which is a result of a project conducted by the Joint Research Centre (JRC) of the European Commission.

Mine drainage can be treated using active processes, which require a continuous input of energy and chemicals to be sustained, and passive processes which do not require energy and uses low resource input once in operation (Martínez et al., 2019). For the LCA analysis performed in this study, CMD from an active mine was considered to be gravity fed to a passive treatment system containing the proposed industrial byproducts. The inputs and outputs of the system are shown in Table 10.

Table 10. Inputs and outputs used for the LCA modeling.

INPUTS	OUTPUTS
<ul style="list-style-type: none"> • Untreated CMD • Industrial byproduct 	Treated CMD

CMD treatment performed by each industrial byproduct was modeled separately using the OpenLCA software and then compared using the project feature of the software. Metal concentrations, sulfate, TOC, nitrate and nitrite data obtained in the batch leaching experiments were used to model the system. Data from individual batch leaching tests obtained in Objective 1 was used to convey the leaching of contaminants from the industrial byproducts themselves. Data from the batch sequential leaching tests in Objective 1 was used to inform the toxic elements present in the untreated CMD and subsequent removal after remediation by each industrial byproduct. Batch SLTs data were used instead of sequential CLTs because the batch tests provided treatment data in worst-case scenarios in which maximal concentrations of contaminants are present in the CMD (compared to lower contaminant concentrations flowing through treatment media over time as seen in CLTs).

Although all the data collected Objective 1 were loaded into the software, the environmental footprint of each proposed treatment was calculated by impact methods built-in the OpenLCA software, which only take into account certain contaminants for each impact category as shown in Table 10. The method ILCD was developed by the JRC of the European Commission was chosen because it takes into account the largest amount of our data. The TRACI method from EPA was chosen because it was developed in the United States and it uses impact factors relevant to our location. The data included in the ILCD and TRACI methods are listed in Table 11 for each impact category analyzed. All contaminants listed in these tables were measured in the batch leach tests in this project; in addition, other water chemistry parameters such as pH, conductivity, sulfate, and chloride as well as other metals including but not limited to Al, B, Ca, Fe, K, Li, Mg, Mn, Si, Sr, and Zn were measured but not included in these analyses as per JRC and EPA guidelines.

Table 11. Lists of contaminants taken into account by the ILCD method developed by Joint Research Centre (JRC) of the European Commission and the TRACI method developed by the US EPA.

Ecotoxicity		Eutrophication		Human Toxicity Carcinogenics		Human Toxicity Non-Carcinogenics	
ILCD	TRACI	ILCD	TRACI	ILCD	TRACI	ILCD	TRACI
Arsenic	Arsenic	Nitrate	Nitrate	Arsenic	Arsenic	Arsenic	Arsenic
Cadmium	Cadmium	Nitrite		Nickel	Cadmium	Barium	Cadmium
Chromium	Chromium			Lead	Lead	Molybdenum	Chromium
Cobalt	Copper			Cadmium	Nickel	Lead	Copper
Lead	Lead			Beryllium		Vanadium	Lead
Nickel	Nickel					Silver	Nickel
Beryllium						Cadmium	
Vanadium						Copper	
Selenium						Beryllium	
Silver						Nickel	
Barium						Chromium	
Molybdenum							
Copper							

Comparisons between the three CMD treatments using the ILCD and TRACI methods to calculate the environmental footprint in the chosen impact categories are shown in Figures 67- 70. As seen in the graphs, RCA has the highest negative effect on all impact categories considered, except for eutrophication. Limestone quarry fines has the highest negative effect on eutrophication due to the high concentrations of nitrate and nitrite leached. The limestone quarry fines performed worse in the human toxicity impact categories for carcinogenics and non – carcinogenics when compared to the stockpiled Sub-Bituminous fly used (Figures 69 and 70). Overall, based on the calculations by the ILCD method, the RCA from pavement waste showed the highest negative effect in the four impact categories considered, whereas the fly ash was ranked best among the three industrial byproducts considered. The results obtained using TRACI were similar to the ones from ILCD, in which RCA performed worse in all impact categories except for eutrophication. Overall, similar to the results obtained through the ILCD method, calculations using the TRACI method showed that the Sub-Bituminous fly ash used had the lowest negative effect in the impact categories tested.

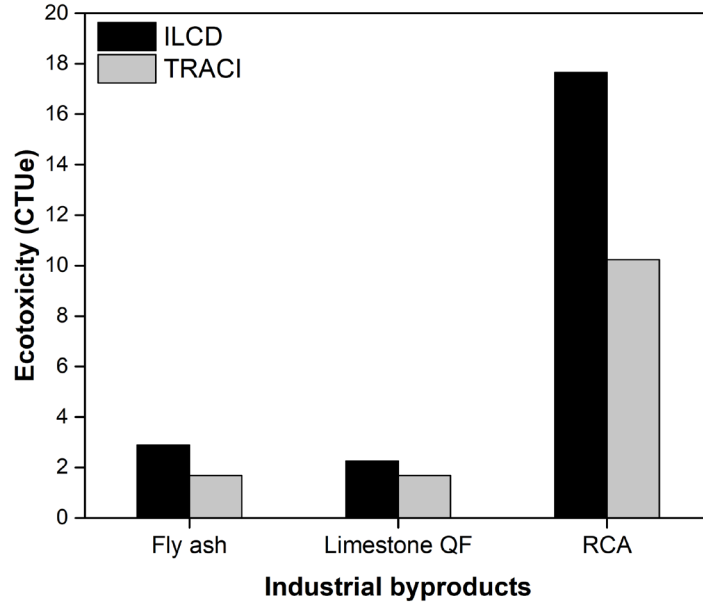


Figure 67. Comparison of the effect of different CMD treatments in the impact category ecotoxicity using the ILCD and TRACI impact analysis methods.

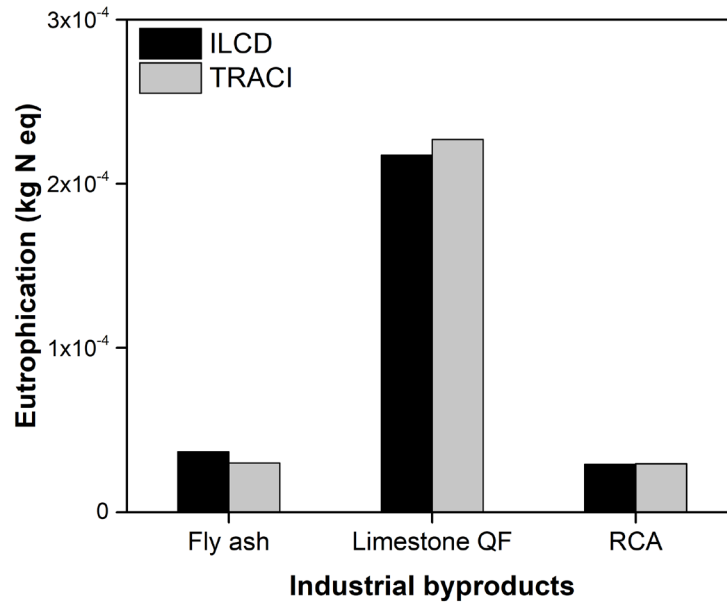


Figure 68. Comparison of the effect of different CMD treatments in the impact category eutrophication using the ILCD and TRACI impact analysis methods.

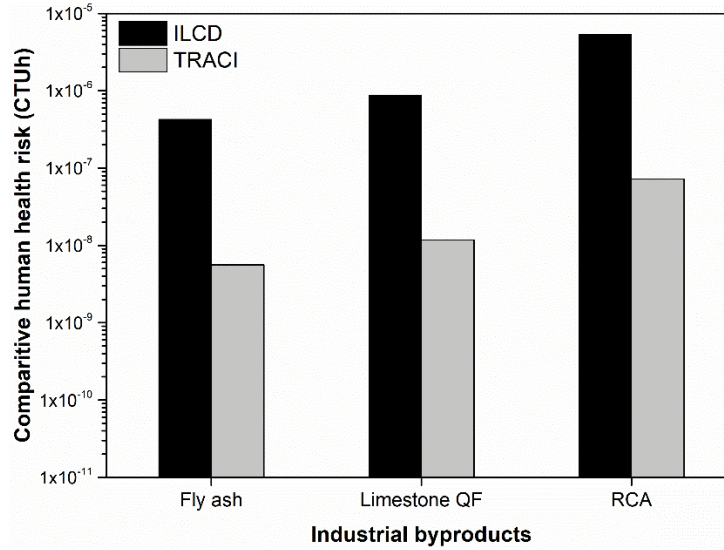


Figure 69. Comparison of the effect of different CMD treatments in the impact category human toxicity carcinogenics using the ILCD and TRACI impact analysis methods.

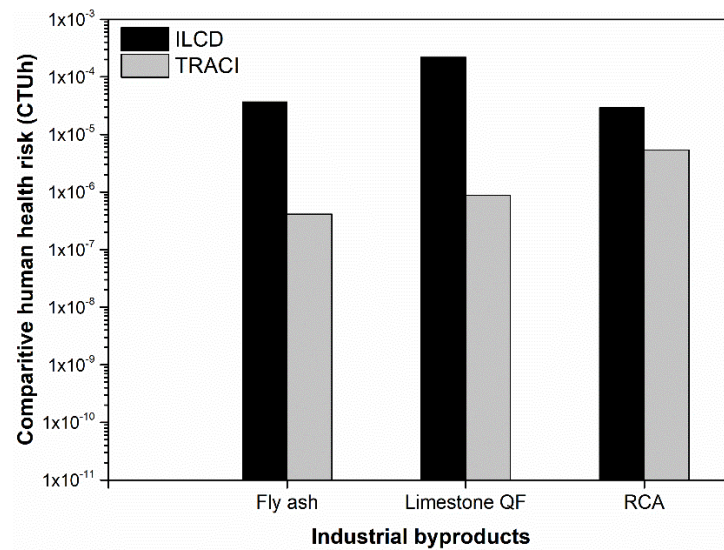


Figure 70. Comparison of the effect of different CMD treatments in the impact category human toxicity non-carcinogenics using the ILCD and TRACI impact analysis methods.

To better visualize the comparison between the industrial byproducts across the different impact categories, relative results are shown in Figure 71, in which the maximum result obtained for each impact category calculated through TRACI is set to 100% and the results of the other variants are displayed in relation to this result.

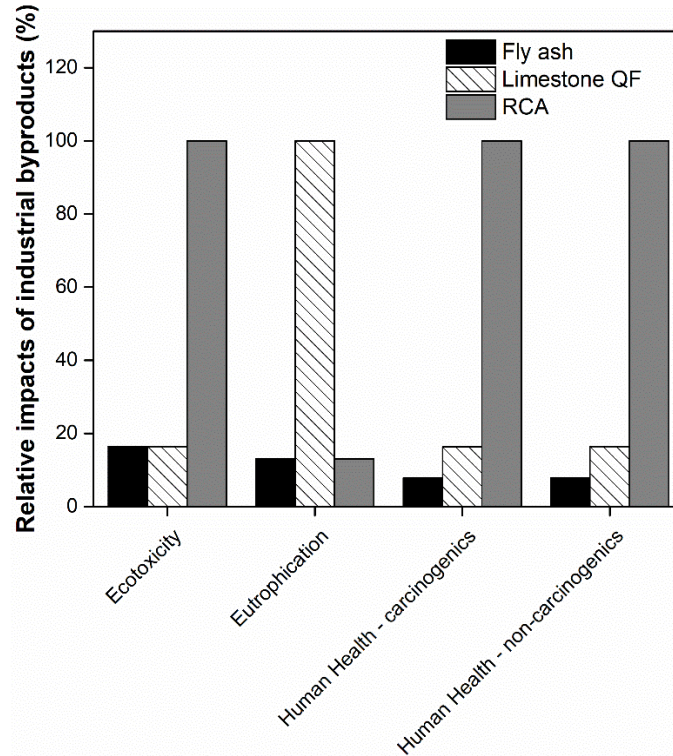


Figure 71. Relative results obtained for each impact categories for all byproducts tested, calculated using the TRACI method.

7.2 Life cycle cost analysis (LCCA)

In order to evaluate the economic feasibility of each proposed CMD treatment, a cost analysis was performed. Similar to the LCA analysis, the LCCA was developed considering the costs to remediate 1 m³ of untreated CMD. For the purpose of this study, we considered the costs associated with the acquisition of the industrial byproduct, landfill disposal post-treatment, and purchase of geotextiles (only used for CMD treatment with fly ash). The amount of industrial byproduct needed by weight is shown in Table 12 and the costs considered for each category are shown in Table 13.

Table 12. Resources needed to treat 1 m³ of untreated CMD.

	Sub-Bituminous Fly ash	Limestone quarry	Pavement RCA
Industrial Byproduct (kg)	32.41	115.17	105.56
Geotextile (ft²)	0.085	-	-

Table 13. Costs associated for each category considered.

	Fly ash	Limestone quarry	Pavement RCA
Cost of Industrial Byproduct (\$/ton)	0*	8	12
Geotextile (\$/100 ft²)	23.5	-	-
Landfill disposal (\$/ton)	40	40	40

*The fly ash used in this study is categorized as off-specification fly ash, which does not possess commercial value.

Based on the data from Tables 12 and 13, the total cost for the treatment of 1 m³ CMD for each industrial byproduct was calculated and is shown in Table 14. Treatment with fly ash is the most effective cost-wise, with a price of \$1.3 dollars/m³ of untreated CMD. The low cost associated with CMD treatment using fly ash is due to the fact that this byproduct poses no commercial value and can generally be acquired for free from power companies (as per personal communication with coal-fired power plant personnel), which currently need to pay to dispose of their off-specification fly ash. In addition, the low density of fly ash decreases the cost of landfill disposal, which is priced by weight of material. It is important to note that in the future, these off-specification fly ashes could gain economic value and not remain free, in which case this LCCA output can change significantly. CMD treatment with limestone quarry and pavement RCA have similar costs (~\$5.5 dollars/m³ of untreated CMD), which is approximately 4 times higher when compared to fly ash (Figure 36). The high costs associated with CMD treatment using RCA and limestone quarry are mainly due to the high density of these materials, which considerably increases the cost of landfill disposal after they have been used up. Even when considering the scenario where the off-specification fly ash would have to be purchased, the fly ash cost by weight needs to be approximately \$130/ton of material in order for the cost of CMD treatment with fly ash to be similar to the costs of treatment with limestone and RCA (~\$5.5 dollars/m³ untreated CMD). Therefore, although the life cost analysis performed in this study was simplified, CMD treatment with fly ash would likely be the most affordable option compared to RCA and limestone quarry.

Table 14. Total cost for each treatment of 1m³ of CMD.

Costs (\$)	Fly ash	Limestone quarry	Pavement RCA
Industrial Byproduct Acquisition	0	0.921	1.266
Geotextile	0.020	0	0
Landfill disposal	1.296	4.607	4.222
TOTAL COST	1.316	5.528	5.489

8. CONCLUSIONS

In this project, we compared the effectiveness of several industrial byproducts for use in remediating CMD. Though the sequential batch WLTs tested the worst-case scenarios for pollution and treatment, the sequential CLTs were the most realistic test setup for assessing the effectiveness of each treatment, especially when considering a similar case as depicted in Figure 76. As such, our recommendations for this treatment scheme are based on results from the sequential CLTs, in which coal wastes were subjected to continuous leaching with water to produce CMD, which was

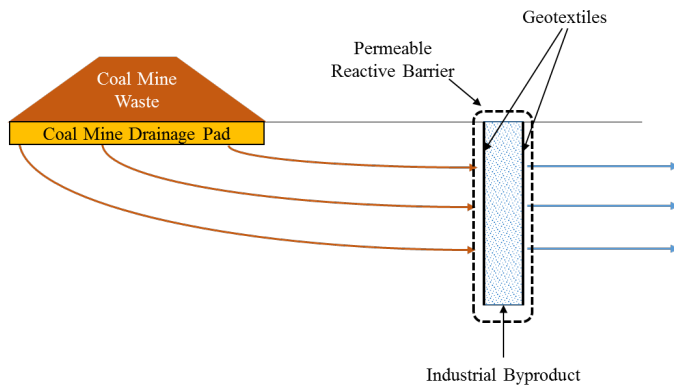


Figure 76. Schematic illustration of coal mine waste with the proposed treatment approach.

then flown into a column packed with industrial byproducts for treatment. Additionally, though there are many water quality parameters that are of concern for environmental and human health, we formulated these recommendations based on the factors that appeared to be most affected by coal waste and/or the industrial byproducts themselves: pH, sulfate, and select metals (As, Be, Cd, Cr, Cu, Li, Mo, Ni, Pb, Se, and V). Environmental impacts and life cycle costs were also taken into account. Table 15 summarizes the findings of this project for the two CMD types tested in the sequential CLTs.

Table 15. Summary of industrial byproducts that were most effective in treating each CMD for each target water quality parameter as well as overall environmental impact assessed through LCA and life cycle costs. Limestone quarry fines (QF), pavement RCA, and stockpiled Sub-Bituminous fly ash from Cedar Rapids, IA (“fly ash”) were considered for this summary.

Parameter	Sub-Bituminous CMD (Newquist)	Bituminous coarse CMD (Sunrise)
<i>pH</i>	Limestone QF	Limestone QF
<i>Sulfate</i>	Pavement RCA	none
<i>As</i>	Pavement RCA	Fly ash
<i>Be</i>	Fly ash	Pavement RCA
<i>Cd</i>	Fly ash	Fly ash
<i>Cr</i>	none	Fly ash
<i>Cu</i>	Fly ash	Fly ash
<i>Li</i>	none	none
<i>Mo</i>	Pavement RCA	Fly ash
<i>Ni</i>	Pavement RCA	Fly ash
<i>Pb</i>	Pavement RCA	Fly ash
<i>Se</i>	Pavement RCA	Fly ash
<i>V</i>	Pavement RCA	Limestone QF
<i>Environmental impact</i>	Fly ash (least impact)	
<i>Life cycle cost</i>	Fly ash (least costs)	

As seen in Table 14, in most cases, the most effective material for treatment depended on the characteristics of the CMD (i.e., from which coal the leachate was generated). Overall, pavement

RCA seemed to treat the CMD from Newquist Sub-Bituminous coal well, whereas the Sunrise coarse Bituminous CMD was treated best with stockpiled Sub-Bituminous fly ash. Though limestone quarry fines did not remove metals well, this material was clearly the most appropriate for pH neutralization of both CMDs. On the other hand, the fly ash materials appeared to have the least negative environmental impacts and the least life cycle costs; as described in Objective 4, these results were based on certain assumptions made about the materials—depending on each situation in which CMD treatment is necessary, other factors may need to be taken into account that could significantly change the environmental and cost impacts.

Looking closely at the data presented in Objectives 1 and 2, it could be concluded that stockpiled Sub-Bituminous fly ash (Cedar Rapids, IA) was the best material for overall treatment of both CMDs tested in this project. Though pavement RCA was more effective in removing some pollutants from Newquist CMD, the fly ash treatments worked almost as well in most cases. It should also be noted that while a geotextile is likely needed for fly ash treatments to ensure that the fine particles do not clog the system, the type of geotextile (woven vs. non-woven) appeared to not affect the treatment efficacy. However, we must consider additional caveats that come with the use of off-specification fly ashes, especially those based on the observations from this study:

- i. Though the fly ash removed some metals well, this material also released a significant amount of some metals (e.g., Li, Mo, V) in the worst-case scenario sequential batch WLTs of most CMDs tested.
- ii. The fly ash treatment significantly increased effluent pH to near corrosive levels (~12).
- iii. While currently inexpensive, the future costs of off-specification fly ash can be difficult to project.

Ultimately, our study shows the use of industrial byproducts for CMD remediation depend on how sensitive the environment surrounding the coal waste site is to perturbations. For example, if there is a water body nearby that has sensitive aquatic ecology and the treated effluent may discharge directly into that water body, it is advised to consider pH neutralization as the first and foremost goal of the treatment—in such cases, the use of limestone quarry fines works best for pH neutralization. It is also noteworthy that while most other water quality parameters tested showed significant increases within ~100 pore volumes (which was equivalent to ~15 days in our CLT setup), pH of the CMD often remained acidic for longer periods of time in the abandoned mine scenarios tested. This observation suggests that perhaps the pH is indeed the most worrisome of the pollution effects from coal waste that we studied in this project. In other scenarios where the treatment effluent will interact with soil first before entering water bodies, off-specification fly ash may be a viable and economical treatment option. In fact, other industrial byproducts tested in this study suitable if the materials are readily available as our results suggest that most of the pollutants tested herein can be further removed in soil.

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