PROGRAM

West Virginia Mine Drainage Task Force Symposium

March 25 - 26, 2014
Morgantown, WV

CO-SPONSORED BY
WEST VIRGINIA MINE DRAINAGE TASK FORCE
AND
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2014 PROGRAM
WEST VIRGINIA MINE DRAINAGE TASK FORCE SYMPOSIUM
Ramada Inn, Morgantown, West Virginia
March 25-26, 2014

Tuesday, March 25, 2014

7:30 – 8:30 a.m. Registration

8:30 – 8:35 a.m. **Welcome and Opening Remarks**
Moderator: Randy Maggard, MEPCO, Morgantown, WV

8:35 – 9:00 a.m. **"Status of West Virginia Mining and Reclamation"**
Lewis Halstead
West Virginia Department of Environmental Protection
Charleston, WV

9:00 – 9:30 a.m. **"An Update of the Appalachian Research Initiative on Environmental Science (ARIES)"**
John Craynon
Virginia Tech
Blacksburg, VA

9:30 – 10:00 a.m. **"Stream Restoration and Mitigation: Requirements of the Army Corps of Engineers"**
Jessica Yeager
Potesta and Assoc.
Charleston, WV

10:00 - 10:30 a.m. **BREAK**

10:30 - 11:00 a.m. **"Stream Restoration Remediation - Designing MTMs to Maximize On-site Stream Reconstruction**
Leslie Hopkinson and John Quaranta
West Virginia University
Morgantown, WV

11:00 – 11:30 a.m. **"Appalachian Ecosystem Restoration: Stream Restoration Techniques"**
Nathan Ober
Civil & Environmental Consultants, Inc.
Bridgeport, WV

11:30 - 12:00 noon **"Predicting TDS Release from Overburden"**
Zenah Orndorff, Lee Daniels, Jeff Skousen and Louis McDonald
Virginia Tech and West Virginia University
Blacksburg, VA and Morgantown, WV

12:00 - 1:30 p.m. **LUNCH**

1:30 - 1: 35 p.m. **REGROUP**
Afternoon Moderator: Ron Hamric, Arch Coal, Morgantown, WV

1:35 - 2:00 p.m. **"2013-14 Legislative Issues on Mining, Reclamation and Water Quality"**
Jason Bostic
West Virginia Coal Association
Charleston, WV

2:00 - 2:30 p.m. **"Selenium Treatment with Iron Oxides at a Surface Mine in WV"**
Paul Ziemkiewicz and Joe Donovan
West Virginia University
Morgantown, WV

2:30 - 3:00 p.m. **"Use of Sulfate-Reducing Mussel Shell Reactors in New Zealand for Treatment of Acid Mine Drainage"**
Dave Trumm and James Ball
CRL Energy Ltd
Christchurch, New Zealand

3:00 - 3:30 p.m. **BREAK**

3:30 - 4:00 p.m. **"Mine Water Treatment Options for Meeting Selenium Regulatory Limits"**
Tom Rutkowski, Rachel Hanson and Kevin Conroy
Golder Associates, Inc.
Lakewood, CO

4:00 - 4:30 p.m. **"Successful Aluminum Treatment: Results of Field Trials"**
Paul Ziemkiewicz and Tom He
West Virginia University
Morgantown, WV

4:30 - 5:00 p.m. **"Factors Influencing Water Discharges from Pennsylvania Underground Coal Mine Pools"**
Anthony Iannacchione
University of Pittsburgh
Pittsburgh, PA

5:00 - 7:30 p.m. **RECEPTION AND EXHIBIT SESSION**

Wednesday, March 26, 2014

8:00 – 8:30 a.m.	**Registration**
8:25 - 8:30 a.m.	**Welcome and Remarks:** Tiff Hilton, WOPEC, Lewisburg, WV
8:30 - 9:00 a.m.	**“Improvements in Fish Populations of Cheat Lake and Cheat River Due to AMD Remediation and Treatment”** Frank Jernejcic West Virginia Division of Natural Resources Fairmont, WV
9:00 – 9:30 a.m.	**“Zeo… What???”** Tiff Hilton, J. Campbell, D. Eyde, J. McEnaney WOPEC Lewisburg, WV
9:30 - 10:00 a.m.	**“Physicochemical and Microbiological Mechanisms of Metals Removal During Passive Mine Water Treatment at Low and Circumneutral pH”** Devin Sapsford Cardiff University Cardiff, Wales
10:00 – 10:30 a.m.	**BREAK**
10:30 – 11:00 p.m.	**“Solving Mine Water Problems with Peat-based Sorption Media”** Paul Eger Global Minerals Engineering Hibbing, MN
11:00 - 11:30 a.m.	**“Passive Bioremediation of Mining Influenced Water Using Sulfate Reducing Bioreactors”** Ilsu Lee, Linda Figueroa, Erick Weiland, and Dan Ramey Freeport-McMoRan Copper and Gold Oro Valley, AZ
12:00 Noon	ADJOURN

WEST VIRGINIA MINE DRAINAGE TASK FORCE SYMPOSIUM

Ramada Inn, Morgantown, West Virginia
March 25 - 26, 2014

ABSTRACTS and PAPERS

An Update on the Appalachian Research Initiative for Environmental Science (ARIES)

John R. Craynon and Michael E. Karmis

ARIES Project Director, Virginia Center for Coal and Energy Research, Virginia Tech, Blacksburg, VA 24061, jcraynon@vt.edu; Director, Virginia Center for Coal and Energy Research and Stonie Barker Professor, Department of Mining and Minerals Engineering, Virginia Tech, Blacksburg, VA 24061, mkarmis@vt.edu

Abstract: The Appalachian Research Initiative for Environmental Science (ARIES) continued to support research into the environmental and community well-being effects of energy production in Appalachia. ARIES researchers have produced over 65 peer-reviewed papers since the program began in March 2011. The industry-supported endeavor, which involves researchers at academic institutions across the Appalachian region, has nearly completed three years of study. The "Environmental Considerations in Energy Production" symposium was held in Charleston, West Virginia in April 2013. The symposium resulted in a peer-reviewed proceedings volume. This presentation highlights some of the recent ARIES research results and discusses the future of ARIES.

Stream Restoration Remediation - Designing MTMs to Maximize On-site Stream Reconstruction

Hopkinson, L.C. and Quaranta, J.D.
Department of Civil and Environmental Engineering
West Virginia University
Morgantown, WV

Abstract

Surface mining reclamation practices in West Virginia result in stable valley fills with planar shape profiles. Environmental concerns related to these engineered structures include the loss of headwater stream length, increased flooding risk, and elevated conductivity and metal levels. One reclamation technique, geomorphic landform design, may offer opportunities to improve aspects of West Virginia valley fill design. The approach designs landforms in a steady-state, mature condition and considers long-term climatic conditions, soil types, slopes, and vegetation. This work will seek to answer the following question: Can stable, landforms be designed such that streams are mitigated or preserved on site, while maintaining the same overall footprint as conventional reclamation? A series of field work was completed to characterize mature landforms in southern WV. These characteristics were used to design landforms for three valley fills of varying size. Ultimately, the research will provide the coal industry and regulators with knowledge to advance reclamation.

Appalachian Ecosystem Restoration;
Stream Restoration Techniques and Case Studies in "Coal Country."

Nathan Ober, P.G.

Civil and Environmental Consultants, Inc.
99 Cambridge Place
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Conference: West Virginia Mine Drainage Task Force 2014 Symposium

Abstract: Ecosystem Restoration in the Appalachian region of the Mid-Atlantic has become synonymous with coal mining for many stream restoration practitioners. Subsurface deep mining and surface mining stretch across the mountainous regions of West Virginia, Ohio, Kentucky, Pennsylvania, and more infrequently in some southern states such as Virginia and Tennessee. Our society has relied upon the extraction of coal as a primary energy resource for decades and the culture in these regions have developed to accommodate this demand. Coal provides our country with affordable energy and often times results in environmental impacts that require mitigation to maintain healthy ecosystems. This type of mitigation is challenging and requires techniques that are unusual and intuitive. West Virginia has developed an in-lieu fee program and mitigation banks to compensate for impacts at offsite locations, however, many of the available sites that are suitable for restoration have historical mining impacts of their own. Therefore, to practice ecosystem restoration in "coal country" we need to understand and except the challenges that exist there. The topics discussed in this presentation will include the challenges and techniques used on streams in Appalachia for subsidence mitigation, high gradient headwater stream restoration along contour (high wall) mining, flow loss mitigation and the use of subsurface liners, and restoration at large scale surface mines.

About the Speakers: Nathan Ober is a geomorphologist and Ecosystem Restoration practice lead for Civil and Environmental Consultants, Inc. As a geomorphologist, Mr. Ober has managed and designed 40+ miles of stream restoration projects, drawing from more than 10 years of experience in fluvial geomorphology, natural channel design, construction management, and post-restoration monitoring. Previously of Stantec, Mr. Ober provided stream assessment and restoration design services, as well as environmental and geotechnical consulting for clients throughout the Southeast and Mid-Atlantic regions.

Predicting TDS Release From Overburden

Zenah Orndorff[1], W. Lee Daniels[1], Jeff Skousen[2], and Louis McDonald[2]
[1] Crop and Soil Environmental Sciences, Virginia Tech
[2] Plant and Soil Sciences, West Virginia University

Overburden in the Appalachian coalfields can affect water quality as runoff or via drainage percolating through valley fills. In particular, over the past decade, concerns about the biological effects of elevated long-term emission of total dissolved solids (TDS) have emerged. By understanding and predicting the leaching potential of mine spoil materials, valley fills can be better designed to minimize environmental impacts. This research program focused on the determination of leaching potentials of 55 coal mine spoils from the Central Appalachian coalfields. Major goals were to characterize the elemental composition of the leachates, to determine the temporal pattern of elemental release, and to compare the results obtained from column leaching trials with larger scale leaching methods and with possible static test predictors. The bulk raw spoil materials were typically near-neutral to alkaline with saturated paste pH values ranging from 4.5 – 8.7. Saturated paste EC values were typically low (<1000 uS/cm), and ranged from 200 – 3800 uS/cm. Most spoil samples contained little or no reactive $CaCO_3$ (as indicated by fizz test) and low total-S (≤0.25%), although a few samples contained up to 1.5% total-S. All materials were leached in columns for 20 weeks (2 leaching events per week) under unsaturated conditions, and the leachates were analyzed for pH, EC, and several ions of concern. A subset of samples also was leached under saturated conditions. Leachate pH typically increased over the first few leach events, and most samples equilibrated at pH 7.5 – 8.5 within 5 to 8 leaching cycles. Highly acidic leachate was observed only from black shale. For many samples, EC decreased notably over the first several leaching events, and achieved a relatively steady state within 18 leach cycles, at which time 80% of the samples were equilibrated to EC levels <500 uS/cm. Samples that exceeded 500 uS/cm throughout the 20 week leaching period were typically finer grained materials, with black shales producing the highest EC. For all rock types, weathered materials equilibrated at lower pH and EC values than their unweathered equivalents. Scaling effects were evaluated for one spoil material by comparing leachate quality from the columns with field-scale barrels (200 L) and large (2.5 m^3) mesocosm tanks. Overall, bulk EC and component elements were similar in levels and temporal response at all 3 scales; however, initial EC levels were higher from the mesocosm tanks, and EC levels in the barrels and mesocosms slowly rose towards the end of the study (likely due to seasonal effects). Preliminary statistical analyses indicate that total-S and saturated paste EC offer promise as predictors of field TDS release potentials; final predictors may involve mixtures of parameters.

Selenium treatment with Iron Oxides at a WV Surface Mine.

Paul Ziemkiewicz and Joe Donovan
West Virginia University
Morgantown, WV

This investigation was a field-scale lysimeter test of the effectiveness of a single basal iron oxide layer at reducing Se mobility in leachate derived from carbonaceous, shaly spoil. The field study at the Hobet mine, Lincoln County, WV, employed fresh surface-mine waste rock layered with an iron oxide amendment obtained from a limestone-treated mine-drainage wetland. The experimental design employed nested amendment concentrations in replication to account for hydrologic and starting-material uncertainties. Thirty lysimeters (4.9 x 7.3 m), each containing 55 metric tons (1.2 to 1.8 m thick) of mine-run carbonaceous shale overburden, were installed at the Hobet mine in SE West Virginia. The fine-grained iron oxide was determined to be primarily metal oxides, 91.5% ferric and 4.36% aluminous, with minor (<3%) SO_4 and Ca, perhaps as gypsum. Based on x-ray diffraction, the mineralogy of the iron was goethite, although residual ferrihydrite may also be present. Various thicknesses of this amendment (0.0064, 0.057, 0.229, and 0.457 m, plus a zero-amendment control) were employed, ranging from 0 to 2.2% weight percent of the spoil. The control and each treatment were replicated 6 times, to estimate uncertainty due to compositional and hydrological variation. Infiltration of rainfall-created leachate that drained to individual batch-collection tanks was sampled 46 times at approximate 2 week intervals from 2010-12. Basal iron oxide layers in the three highest amendment categories removed up to 76.1% selenium (in comparison to unamended piles) from leachate by adsorption. Only lysimeters with very thin iron oxide layers showed no significant reduction compared to unamended piles. Reproducibility of replicates was within acceptable limits for both amended and unamended lysimeters. Results indicate that in-situ amendment using iron oxide obtained from treatment of mine water can sequester Se by adsorption on surfaces of goethite and possibly also ferrihydrite. This process is demonstrated to substantially reduce dissolved Se in leachate. The general technique of using iron-oxide sludges or similar waste materials as an absorbent for Se at mine sites is novel and merits study for further implementation. These results are being examined in the context of historical Se observations at this mine to develop a strategy to improve compliance with regulatory discharge limits until natural long-term exhaustion of the Se source occurs.

Use of sulfate-reducing mussel shell reactors in New Zealand for treatment of acid mine drainage

D. Trumm[1] and J. Ball[1]
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ABSTRACT

Green-lipped mussels *(Perna canalicula)* is the largest seafood export from New Zealand, producing large amounts of shell waste which ends up in landfills. Since 2007, researchers and practitioners have experimented with the use of mussel shells to treat acid mine drainage (AMD) in New Zealand. In some cases, the mussel shells replace the limestone in a typical sulfate-reducing bioreactor, and in other cases reactors are built with only mussel shells. The reactors with just the mussel shells also include the associated waste mussel meat, which accounts for about 10% by mass. This mussel meat provides an organic substrate for sulfate-reducing bacteria, creating a reducing environment where metals are removed as sulfides. Until now, these systems have been constructed with vertical downward flow. When oxic AMD flows into a system, dissolution of the shells results in precipitation of iron hydroxides on the top of the reactor, which can eventually reduce permeability of the system. Reducing reactions occur deeper in the system, resulting in the formation of sulfides from trace elements such as zinc and nickel.

In this study, three small-scale mussel shell reactors were constructed in series at an active coal mine site to treat AMD. Each reactor was constructed with an upflow configuration in an attempt to establish reducing conditions and prevent the formation of iron hydroxides. Inlet was chemistry was: Fe (108 mg/L), Al (28 mg/L), Mn (24 mg/L), Zn (6.3 mg/L), Ni (1.4 mg/L), and sulfate (2100 mg/L). Residence times ranged from 14 to 232 hours in each system. The pH was raised to near 8 through the reactors and net alkalinity was produced. Metal removal rates were as follows: Fe (96 to >99%), Al (>99%), Ni (95 to >99%), Zn (98 to >99%), and Mn (0 to 22%). With the exception of Mn, these metals were mostly removed in the first reactor. Sulfate concentrations decreased by up to 500 mg/L, dissolved sulfide increased by approximately 60 mg/L, DO concentrations decreased from near saturation to less than 1%, and ammoniacal nitrogen increased through the systems, all suggesting that reducing conditions were achieved in the systems. It is likely that Fe, Zn, and Ni were removed as sulfides, Al as hydroxides, and Mn as hydroxides or carbonates. A yellowish-white crystalline and amorphous precipitate forming on the surface of the reactors may be elemental sulfur. These results suggest that upflow configurations may be a useful construction technique for mussel shell reactors.

INTRODUCTION

The green-lipped mussel *(Perna canalicula)* is the largest seafood export from New Zealand. The aquiculture industry produces over 140,000 tons of shells annually (Aquaculture New Zealand 2010). Native to New Zealand, much of the export is fully shelled mussels, which produces a large amount of shell waste. Although some of the waste is used as a lime amendment by the agricultural industry, much of it ends up in landfills.

Since 2007, various researchers have used waste mussel shells to treat acid mine drainage (AMD) in laboratory experiments, small-scale field trials, and large-scale systems in New Zealand. Mussel shells provide a source of alkalinity, and the associated waste mussel meat and other sea life (about 10% by mass) provide organic material for sulfate-reducing bacteria. In the initial early laboratory experiments, the mussel shells were used as a replacement for limestone in typical sulfate-reducing bioreactors containing other sources of organic matter, such as compost, bark chips, and post peel waste strips (McCauley et al. 2009, Mackenzie 2010, Mackenzie et al. 2011).

Later, large-scale field reactors were constructed with only mussel shells and their associated waste mussel meat. These reactors perform well, removing 96-99% of iron, aluminum, nickel, and zinc and restoring pH from <3 to >7 (Crombie et al. 2011). Autopsy work by Diloreto et al. (in press 2014) show that the metals are sequestered in distinct zones and in distinct forms within the reactors. The upper layer is dominated by a thick iron hydroxide precipitate, followed by a transition zone, below which is an aluminum hydroxide layer. Zinc sulfides and nickel sulfides are present below the aluminum layer. Mussel shells are nearly completely dissolved away near the surface, becoming more abundant with depth. Redox measurements (Eh) show a change with depth, from oxidizing conditions in the upper layers changing to reducing conditions within and below the aluminum hydroxide layer. The pH increases with depth, reaching neutral where shells are most abundant.

Performance of the mussel shell reactors over time is largely unknown. It is likely that the transition zone where conditions change from oxidizing to reducing migrates downward with time as the mussel shells are dissolved. If so, zinc and nickel sulfides precipitated in these layers may be oxidized and the metals released as the dissolution front migrates downward. The iron oxide and aluminum layers would likely dominate the system with time, potentially reducing permeability and the system would fail once all the mussel shells have been dissolved.

All the previous systems (laboratory and field trials) were constructed with downflow configurations. In our current study, we have constructed field-trial mussel shell reactors with an upflow configuration to determine if reducing conditions would predominate over oxidizing conditions throughout the reactors, and if iron would precipitate as a sulfide rather than as a hydroxide. In addition, increased bicarbonate alkalinity generation in a fully reducing system may slow shell dissolution rates, increasing the lifespan of the systems.

METHODS

Three passive treatment systems were constructed using 1000 L plastic tubs (standard intermediate bulk containers) with PVC piping, alkathene piping and associated valves, and were installed at an active coal mine in New Zealand to treat AMD. Each system was filled with waste mussel shells from the fishing company Sandford Limited. The mussels were freshly harvested and contained approximately 10% waste mussel meat, which included remnants of the Green-lipped mussels and whole black-shell mussels. Most shells were broken into pieces approximately 5 cm long (Figure 1).

Figure 1. Mussel shells in completed mussel shell reactor prior to filling with water.

The systems were installed in series with an upflow configuration, such that the inlet was at the base of each system and the water flowed upwards through the shell bed driven by sufficient hydraulic head. Sampling ports were located at the inlet to the three systems, between systems one and two, between systems two and three, and at the outlet from system three. Each system was covered with a tarp to exclude rainfall and sunlight.

The systems operated for a period of 141 days. Flow rates were varied to determine metal removal for different hydraulic residence times (HRTs). Inlet and outlet samples were collected fortnightly from each system and analyzed for dissolved iron (Fe), aluminum (Al), manganese (Mn), nickel (Ni), zinc (Zn), and calcium (Ca), nitrogen species, dissolved reactive phosphorous, sulfate, and dissolved organic carbon at a New Zealand laboratory using inductively coupled plasma mass spectrometry, colorimetry, ion chromatography, catalytic oxidation, and cadmium reduction techniques. Field measurement included pH, dissolved oxygen, and sulfide.

RESULTS

Flow rates ranged from 40 to 660 ml/min through the system train, equating to HRTs ranging from 14 hours to 232 hours in each of the first two systems. The third system had slightly fewer mussel shells, resulting in a nine percent lower residence time compared to that in each of the first two systems.

The inlet AMD chemistry is dominated by sulfate (2100 mg/L), Fe (108 mg/L), Al (28 mg/L), and Mn (24 mg/L), with low concentrations of Zn (6.3 mg/L) and Ni (1.4 mg/L). The pH ranges from 2.9 to 3.1. Typically, Fe(II) comprises five percent of the total Fe, dissolved oxygen is near saturation, and no dissolved sulfide is present.

As the water passes through the systems, the following metal removal rates are achieved: Fe (96 to >99%), Al (>99%), Ni (95 to >99%), Zn (98 to >99%), and Mn (0 to 22%) (Figure 2).

Several parameters suggest that reducing conditions are being achieved in the systems. Sulfate concentrations lower through the systems (by up to 500 mg/L) while dissolved sulfide concentrations increase (by approximately 60 mg/L) (Figure 3). Dissolved oxygen concentrations decrease from near saturation to below 1% in the first reactor and ammoniacal nitrogen (reduced nitrogen) concentrations increase linearly through the three systems. The pH increases from 3 to 7.5 in the first reactor and shows some increase to near 8 through the second and third reactors (Figure 4). Concentrations of calcium (Ca) increase predominantly in the first reactor, while alkalinity follows a linear trend through the three systems.

After the systems had operated for several months, precipitates were noted on the surface of the water in all three reactors (Figure 5). In the first two, this precipitate exhibited a vein-like and crystalline-like texture with various colors of grey and tan. In the third reactor it was dominated by yellowish-white crystalline and amorphous material.

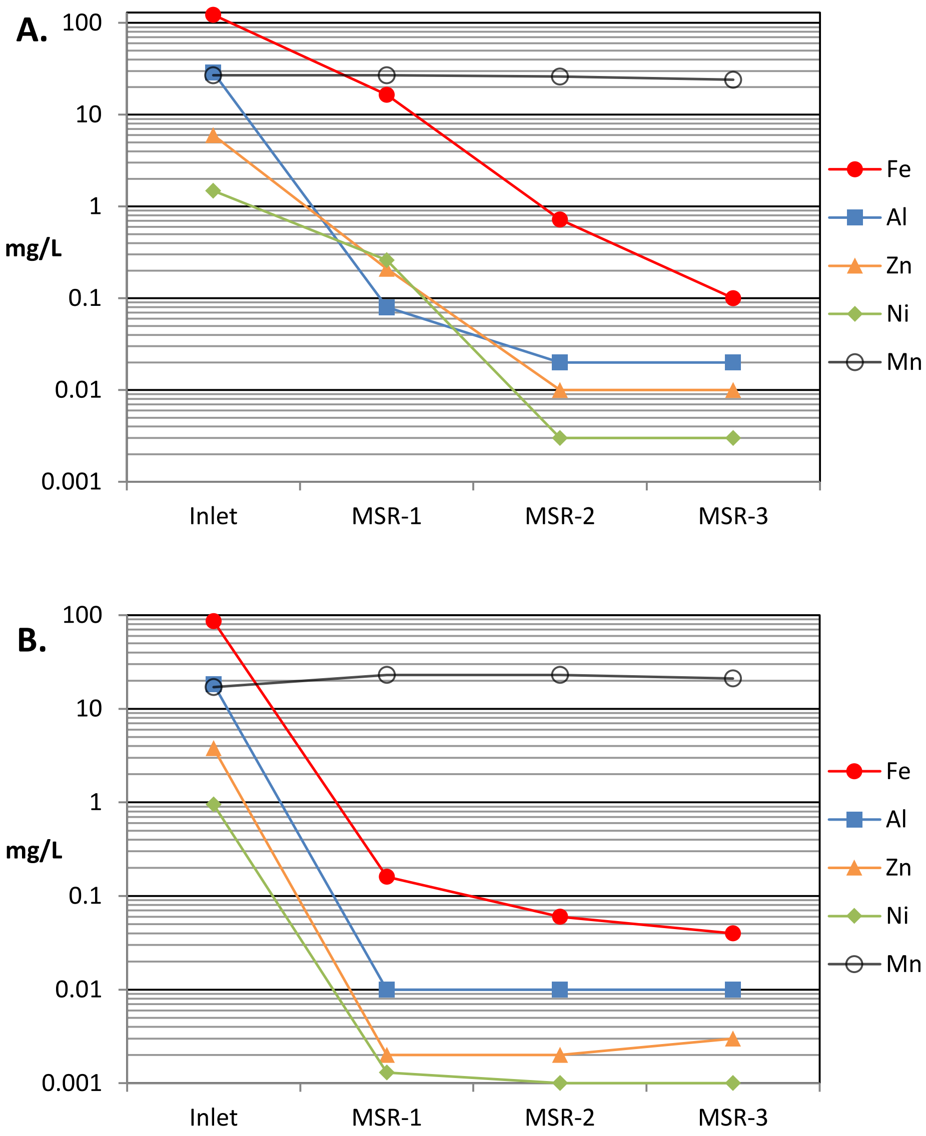

Figure 2. Concentrations of metals through treatment system. **A.** HRT of 28 hours. **B.** HRT of 95 hours. MSR-1, mussel shell reactor 1; MSR-2, mussel shell reactor 2; MSR-3, mussel shell reactor 3.

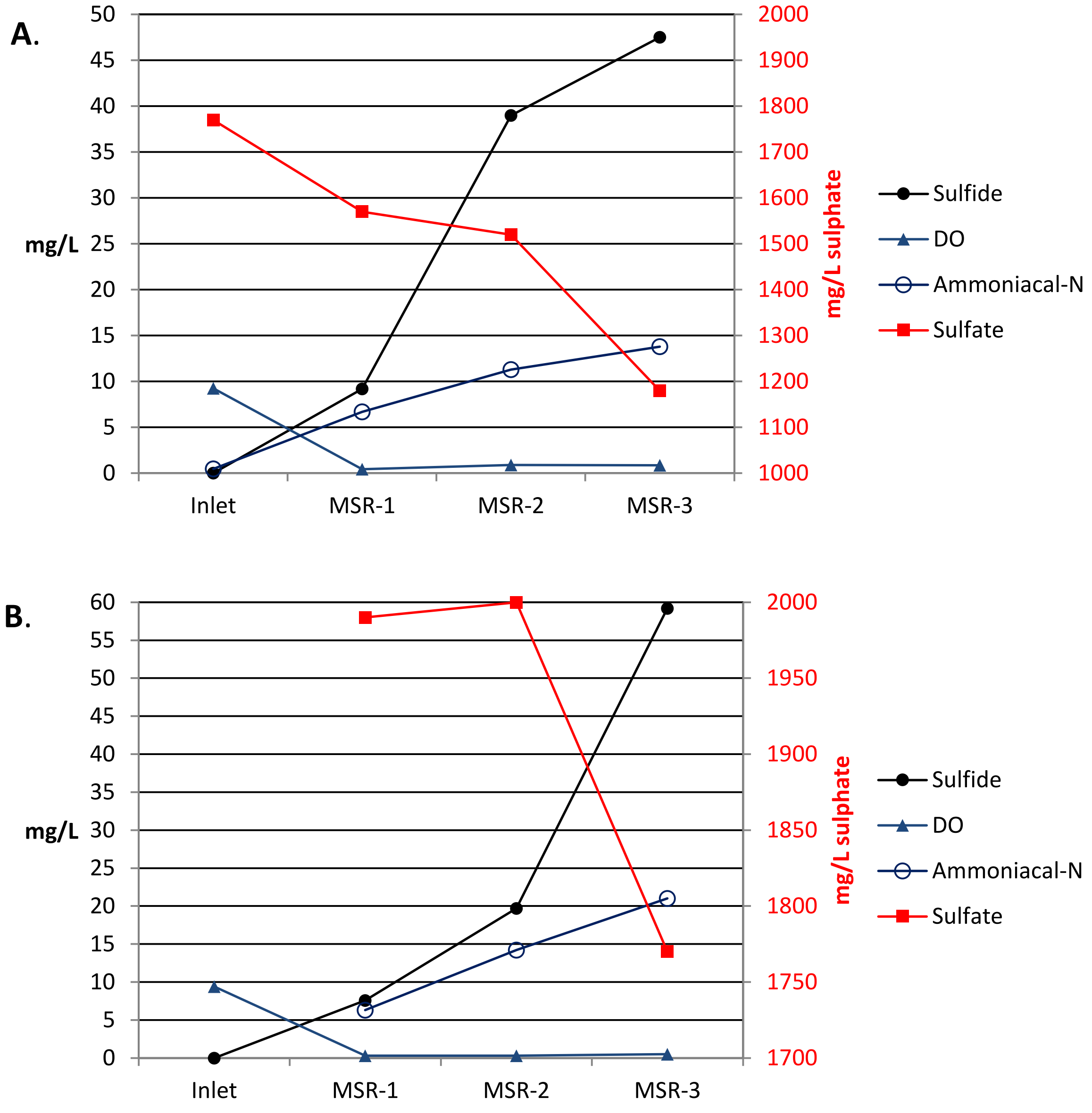

Figure 3. Concentrations of sulfate, sulfide, DO, and ammoniacal nitrogen through treatment system. **A.** HRT of 56 hours. **B.** HRT of 95 hours. MSR-1, mussel shell reactor 1; MSR-2, mussel shell reactor 2; MSR-3, mussel shell reactor 3.

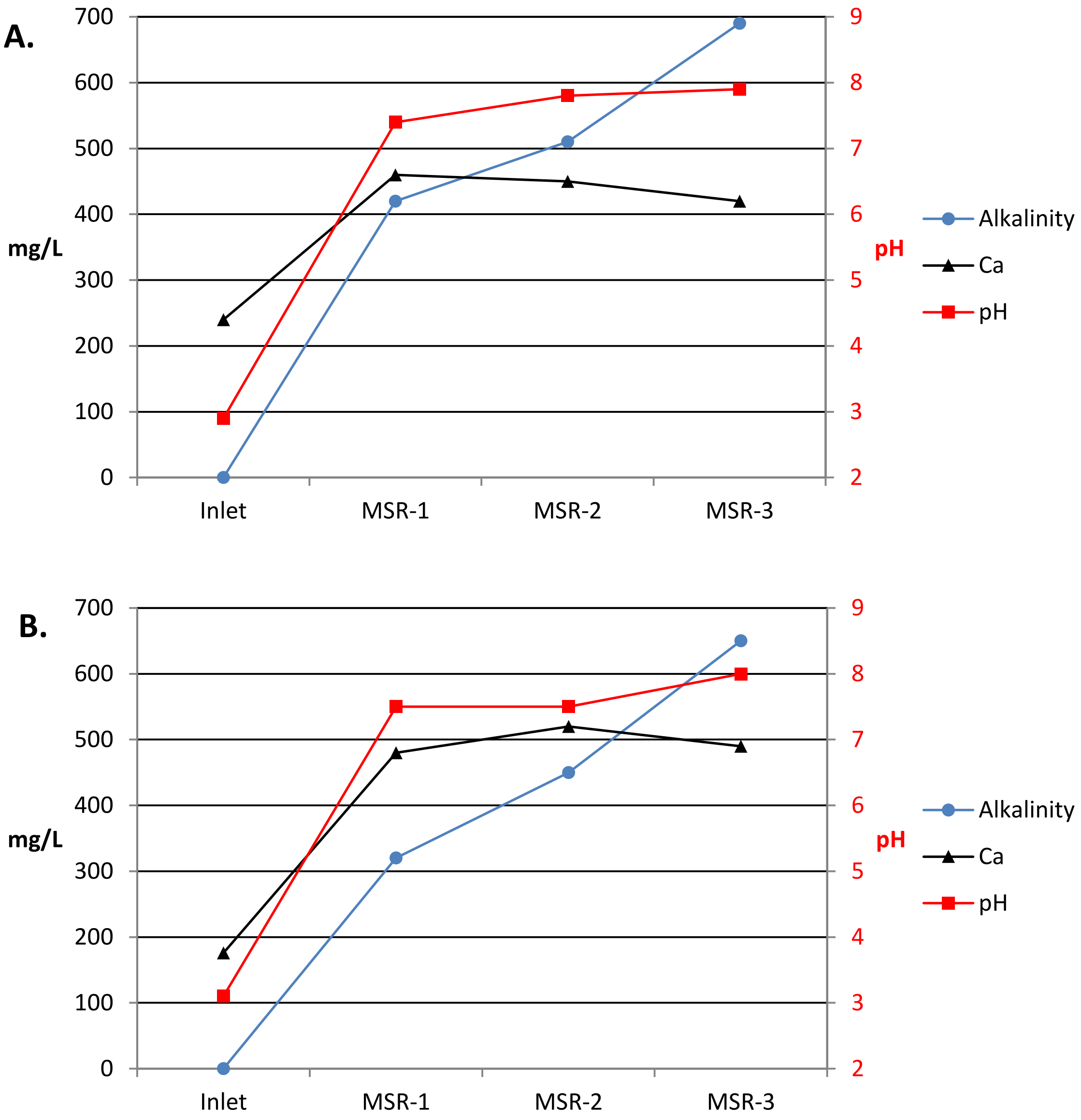

Figure 4. The pH and concentrations of alkalinity and calcium through treatment system. **A.** HRT of 56 hours. **B.** HRT of 95 hours. MSR-1, mussel shell reactor 1; MSR-2, mussel shell reactor 2; MSR-3, mussel shell reactor 3.

Figure 5. Precipitates on the water surface of mussel shell reactors.

DISCUSSION

Neutralization of the AMD and generation of bicarbonate alkalinity is likely occurring through both dissolution of the mussel shells and sulfate reduction by sulfate-reducing bacteria. Almost all of the metal removal by the systems and pH increase is accomplished in the first reactor, with the exception of Mn which shows removal (albeit minimal) in the second and third systems. Changes in dissolved oxygen, ammoniacal nitrogen, and sulfate show that reducing conditions are established in the first reactor, and are enhanced in the second and third reactors, suggesting that the transition metals Fe, Ni, and Zn are likely being removed as sulfides.

Aluminum, however, does not form a sulfide in these systems, but rather precipitates as a hydroxide. Manganese also does not form a sulfide in these systems, but rather can precipitate as oxides, hydroxides (Stumm and Morgan 1996), and carbonates (Bamforth et al. 2006) and can be removed through adsorption onto iron hydroxides. It is unlikely that manganese oxides are forming under these reducing conditions and unlikely that Mn is being adsorbed onto iron hydroxides if most of the Fe is being removed as sulfide. It is possible that the minimal removal of Mn through these systems is occurring through the formation of manganese carbonates, similar to rhodochrosite ($MnCO_3$) or kutnahorite ($CaMn(CO_3)_2$. The formation of these minerals typically requires a pH of greater than 8, which is approached in the third system.

In the second and third reactors, additional alkalinity is produced, the pH is raised slightly higher, and sulfate concentrations are lowered significantly while dissolved sulfide concentrations increase. Minimal dissolution of mussel shells occurs in the second and third reactors, as evidenced by relatively stable Ca concentrations. Therefore, the increase in bicarbonate alkalinity in the second and third systems is likely due to sulfate reduction by sulfate-reducing bacteria. The precipitates forming on the surfaces of the reactors may be elemental sulfur, since more sulfate is removed from these systems than can be accounted for by dissolved sulfide and the formation of metal sulfides.

The construction of these three systems in series creates a true plug flow reactor (Schmidt and Lanny 1998). Although short-circuiting is possible within each individual component, short-circuiting through the entire system train is prevented by having three distinct parts to the system. Since sampling can be conducted between each component of the system, the performance and removal mechanisms in each component can be analyzed separately and extrapolated to the potential performance of a full scale system. Construction of trial passive treatment systems in series can provide useful information on treatment performance and metal removal mechanisms.

The upflow configuration likely contributes to the successful establishment of reducing conditions and likely will lead to minimal formation of iron hydroxides. It is preferable to avoid the formation of iron hydroxides, as this would lead to a decrease in permeability with time, as was noted in a large-scale mussel shell reactor constructed at Stockton Mine, West Coast, New Zealand (Crombie et al. 2011).

Additional upflow mussel shell reactors have been constructed at the Bellvue abandoned coal mine AMD site on the West Coast of New Zealand (West et al. 2013). Along with mussel shell reactors, a bioreactor containing compost, bark chips, post peel strips, and mussel shells is operating at the Bellvue site to compare the performance of mussel shells with and without an organic matrix. The results from Bellvue and from this study will be used to optimize mussel shell reactor design for other sites in New Zealand.

CONCLUSIONS

1. Three small-scale mussel shell reactors were constructed in series at an active coal mine in New Zealand to treat AMD. Unlike previous mussel shell reactors in New Zealand, these were constructed in an upflow configuration.
2. Inlet water chemistry to the system train had a pH of 2.9 to 3.1, and metal concentrations as follows: Fe (108 mg/L), Al (28 mg/L), Mn (24 mg/L), Zn (6.3 mg/L), and Ni (1.4 mg/L). Sulfate concentrations were 2100 mg/L.
3. Residence times in each of the three reactors ranged from 14 to 232 hours, over an operating period of 141 days.
4. The pH increased to 7 through the first reactor and near 8 through the second and third reactors and the effluent water had net alkalinity.
5. Metal removal rates were as follows: Fe (96 to >99%), Al (>99%), Ni (95 to >99%), Zn (98 to >99%), and Mn (0 to 22%). With the exception of Mn, these metals were mostly removed in the first reactor.
6. Sulfate concentrations were lowered by up to 500 mg/L, dissolved sulfide increased by approximately 60 mg/L, DO concentrations decreased from near saturation to less than 1%, and ammoniacal nitrogen increased through the systems, all suggesting that reducing conditions were achieved in the systems by means of sulfate-reducing bacteria.
7. It is likely that Fe, Zn, and Ni were removed in the system as sulfides, Al as hydroxides, and Mn as hydroxides or carbonates.
8. A crystalline and amorphous precipitate forming on the surface of the reactors may be elemental sulfur.
9. An upflow configuration through mussel shell reactors may help to establish and maintain reducing conditions and remove Fe as sulfides rather than hydroxides, thereby maintaining permeability and extending the longevity of these systems.

ACKNOWLEDGEMENTS

This research was financed by the Ministry for Business, Innovation and Employment, Contract CRL1202. The mussel shells were donated by Sanford Limited, Christchurch. We acknowledge the anonymous mining company which allowed the systems to be constructed at their mine site. Preparation of graphs was completed by Patrick Turner of CRL Energy.

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Mine Water Treatment Options for Meeting Stringent Selenium Regulatory Limits

Tom Rutkowski[1], Rachel Hanson[2], Kevin Conroy[3]

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Abstract

Selenium can be a constituent of concern in mine waters and is often present in neutral waters. Selenium is typically leached from waste rock piles as the selenate ion and mines can be faced with multiple, high-flow contaminated discharges. In recent years, biological treatment has emerged as an effective and relatively inexpensive method compared to physical and chemical methods. With some waters, biological treatment alone is sufficient to achieve stringent regulatory limits; however, in other cases, additional unit processes are required. Three treatment cases studies are included for treating moderate levels of influent selenium (50 – 500 µg/L).

Key words: selenium, biological, water treatment

Factors Influencing Water Discharges from Pennsylvania Underground Coal Mine Pools

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Abstract

The Surface Mining Control and Reclamation Act of 1977 requires underground coal mines with acid- or iron-producing strata to prevent discharges. In Pennsylvania, engineered barriers are designed to prevent discharges to surface waters, primarily from contained mine pools. In many cases, mine layout designs focus primarily on the size and hydraulic performance of the un-mined coal barrier between the up-dip mine pool and areas where down-dip surface discharge is possible. In other cases, designs focus on preventing discharges from barriers contained within the strata surrounding the mined coalbed.

This Appalachian Research Initiative for Environmental Sciences (ARIES) sponsored research effort is focused on identifying the factors responsible for barriers that have performed successfully, as well as those that have not. Nine case studies are analyzed providing an opportunity to examine a diverse set of conditions, both from a geologic and mining standpoint. While the exact causes for the successes and failures could not always be determined, reasonable mechanisms are presented. Important factors include: mine layouts (coal barrier size), mining methods (extraction ratio), hydraulic head and conductivity (interaction of both conditions), geology (strength variations), and overburden. These factors are used to identify risk to barrier design.

Improvements in the fish populations of Cheat Lake and Cheat River in response to reductions in acid mine drainage pollution from AML reclamation work and mine drainage treatment.

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Over a century of coal mining in the Cheat River watershed in northern West Virginia resulted in abandoned coal mines that have generated massive amounts of acid mine drainage (AMD) and depressed or eliminated fish populations in Cheat River and Cheat Lake. However, at least 200 land reclamation and water treatment projects have been completed since 1994 in order to reduce AMD in the Cheat watershed and restore fish populations.

A rotary drum neutralization station was constructed on Blackwater River in the upper Cheat watershed in 1994. This restored 4 miles of trout water on the Blackwater River and provides some alkalinity to the Cheat River. Fish surveys at Seven Islands on Cheat River downstream of the Blackwater in 1959, 1973, 1980, and 1999 produced standing crops (SC) of 60, 27, 21, and 58 lbs/acre. Historic AMD input from Blackwater River and improvements from neutralization in 1994 are reflected in this data. Three additional surveys over a 26-mile reach downstream of Seven Islands in 1999 documented a 69% decrease in SC from AMD. Farther downstream, a sport fishery had been non-existent since 1970. This 14-mile reach upstream of Cheat Lake is inaccessible for traditional survey techniques, but can be characterized by angling. One angler's float trip in this lower reach during 1997 produced one yellow perch (*Perca flavescens*). Four similar trips in 2005 produced 132 fish of seven species (76% smallmouth bass, *Micropterus dolomieu*) that substantiated improvements in water quality. Smallmouth bass now constitute the sport fishery in most of the Cheat River mainstem.

Fishing in Cheat Lake, which is located at the bottom of the Cheat watershed, has improved over the last 23 years. From the 1960s to the late 1980s, Cheat Lake's sport fishery was essentially non-existent due to AMD. Fish monitoring since 1997 indicates that species composition once dominated by acid-tolerant bullheads (*Ameiurus* species) has shifted and is now more diverse. Thirty-eight species have been collected and channel catfish (*Ictalurus punctatus*), black bass (*Micropterus punctulatus*, *M. salmoides*, *M. dolomieu*), and yellow perch are abundant. A walleye stocking and telemetry project is now in progress. Consequently, Cheat Lake is now a destination for bass tournaments and recreational anglers. Improved fish populations and angling success is directly related to AMD reduction in the watershed.

In 2006, Congress reauthorized the AML program under the 1977 Surface Mining Control and Reclamation Act. The reauthorization provided increases in the amount of money released to states for reclaiming abandoned coal mines and for AMD amelioration projects. Without adequate funding for continuing AMD treatment, fish populations and angling opportunities in Cheat River and Cheat Lake will decline, potentially to pre-AMD treatment levels. This program has been and will continue to be the major factor in maintaining and enhancing fish populations in the Cheat watershed. Without congressional intervention, the AML program is now set to expire in approximately 9 years.

Zeo What????

By--T. Hilton, J. Campbell, D. Eyde, J. McEnaney

"A long time ago in a galaxy far, far away" (Anjean, West Virginia), a lady by the name of Jo Davison contacted me and said after studying bacteria for many years in the Okefenokee swamp, she had developed a method by which she could remove metals from mine drainage using her bugs. She visited one of my treatment sites where I was removing iron with ammonia, coagulants, and flocculents and declared that her Bio-Carb with special bacteria and other secret ingredients, would replace the chemicals. However, she warned me that before her bugs (she called them sinkers-swimmers-& floaters) could survive and multiply, the ammonia that was present in the water had to be removed. To accomplish this, she told me to obtain some Zeolite, in which my immediate response was—Zeo What, and the rest is history.

Twenty five years passed before I heard the word Zeolite again. I was doing consulting work for Greenbrier Smokeless Coal Co. in Greenbrier County, West Virginia, when they were purchased by Coronado Coal Co. on April 1, 2013. In the course of general conversation with one of the Coronado Coal management, he informed me that he owned a Zeolite mining operation by the name of St. Cloud Mining Company. Just the mention of Zeolite, took me back 25 years to the "Bug Lady", Jo Davison. One thing led to another and I asked if he could send me some Zeolite to conduct testing on in regards to how it might be used for mine drainage remediation. As previously stated, when Jo introduced me to Zeolite, her explanation of Zeolite was that the material was utilized in aquarium filters and hatchery's to remove urine generated ammonia, from the water for obvious fish toxicity reasons. My current knowledge of Zeolite was limited to what she had told me and I did not know how it might work when subjected to mine drainage. Therefore, it seemed as if it were time to at least attempt to understand the general water chemistry properties associated with Zeolite if any productive results were to come from testing. To that end, Wikipedia was my first stop, followed by the St. Cloud Mining website (www.stcloudmining.com) in hopes they might have understandable information for non-techies as myself. As such, please bear with me for a moment or two while I regurgitate some information from both sites to provide some general information

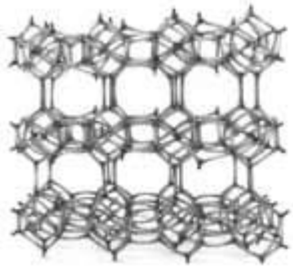
Wikipedia—What is Zeolite?

"**Zeolites** are microporous, aluminosilicate minerals commonly used as commercial adsorbents.[1] The term zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been adsorbed by the material. Based on this, he called the material *zeolite*, from the Greek ζέω (*zéō*), meaning "to boil" and λίθος (*líthos*), meaning "stone"."

"Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins."

www.stcloudmining.com--What is Zeolite?

"Generally speaking, natural zeolites are hydrated aluminosilicates. They consist of an open, three-dimensional cage-like structure and a vast network of open channels extending throughout. Loosely bound, positively charged atoms called cations, are attached at the junctures of the negatively charged aluminosilicate lattice structure. The aluminosilicate framework provides exceptional strength and stability to the lattice structure.



The channels, typically 0.3 to 0.7 nanometers in diameter (3 to 7 angstroms, slightly larger than a water molecule), selectively screen molecules according to size and exchangeable cations. Molecules too large to pass through the entry channel are excluded, thus giving rise to the term "molecular sieve".

The molecular structure, surface area, surface charge density, and cation exchange capacity (CEC) of each particular zeolite will determine its loading, shrinking, swelling and stability under various conditions. Zeolites have a rigid, three-dimensional crystalline structure (similar to honeycomb) consisting of a network of interconnected tunnels and cages. Zeolites in general have high specific surface areas and their rigid framework limits shrinking and swelling.

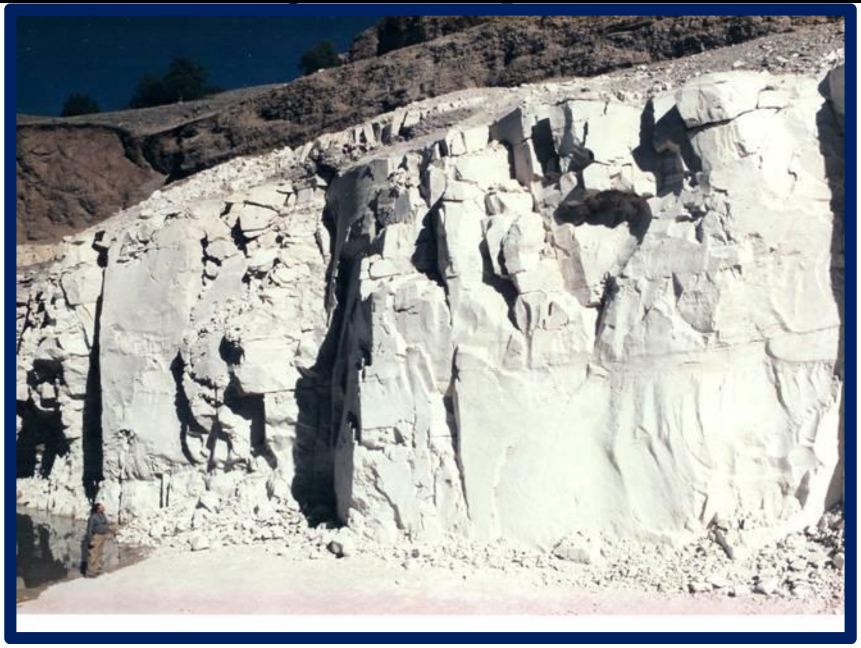
One Final Reference

WOPEC—What is Zeolite?

Zeolite is a **MBBAR** (short for **"Mind Blowing Bad Ass Rock"**) that removes iron, aluminum, and manganese without producing any sludge, while simultaneously raising low pH mine drainage by removing hydrogen ions and lowering high pH's of over-treated water generally associated with manganese removal. Also, it will remove certain cations responsible for creating high Dissolved Solids and/or high Osmotic Pressure.

You are probably curious as to what Zeolite looks like, so prior to proceeding with the test results, here are a few photos.

St. Cloud Mining Zeolite Deposit in New Mexico



St. Cloud Mining Processing Plant—Winston, New Mexico

Zeolite Final Product after Mining-Crushing-Screening

To validate the claim by WOPEC that Zeolite is **MBBAR *certified*,** several different types of laboratory tests were conducted to look at various mine drainage types and their particular reaction when put in contact with Zeolite. This paper presents the results of these tests, and hopefully offers those with certain type of mine drainage effluent problems, some hope in regards to an affordable solution.

Test No.1—Does Zeolite do anything?

Initially, even though I read a few non-AMD related technical papers on Zeolite, there was nothing that indicated what it would do with our AMD type chemistry. I was working on some pretty tough water for a client and decided to do a simple test to find out if there was any reason to pursue additional testing. I took 3-1,000 ml cylinders and filled them with ¼” X ½” zeolite. I had water from three different sites, which was used to fill the cylinders. Each cylinder accepted about 450 ml of water, resulting in 45% pore space.

<u>**This was the Zeolite used for the initial tests.**</u>

The raw water analysis for the three test samples was as follows:

Parameter	Sample 1	Sample 2	Sample 3
pH	**3.31**	**2.97**	**2.52**
Dissolved Iron	**2.48**	**9.23**	**617.20**
Dissolved Manganese	**32.23**	**53.13**	**29.34**
Dissolved Aluminum	**48.82**	**52.24**	**109.80**

After a few hours of contact time with the Zeolite, the resulting water quality was was rather "Mind Blowing", which accounted for the first part of the official WOPEC----**MBBAR** ***certification***.

Sample 1

Parameter	Raw Water	After Zeolite
pH	**3.31**	**5.71**
Dissolved Iron	**2.48**	**0.21**
Dissolved Manganese	**32.23**	**8.27**
Dissolved Aluminum	**48.82**	**0.11**

Sample 2

Parameter	Raw Water	After Zeolite
pH	**2.97**	**5.32**
Dissolved Iron	**9.23**	**0.22**
Dissolved Manganese	**53.13**	**14.83**
Dissolved Aluminum	**52.24**	**0.46**

Sample 3

Parameter	Raw Water	After Zeolite
pH	**2.52**	**4.00**
Dissolved Iron	**617.20**	**46.60**
Dissolved Manganese	**29.34**	**30.01**
Dissolved Aluminum	**109.80**	**12.05**

For those of you who always try to find the bad in everything, you are right. The resultant water quality did not meet any particular N.P.D.E.S. limits, but that was not the purpose of this test. The purpose was to see if the Zeolite would do anything at all, and "**wow**", did it ever. It's obvious from the results in the previous charts, that Zeolite loves iron and aluminum and likes manganese depending upon the prevailing cation competition it faces. It also has a great affinity for hydrogen ions as seen by the increase in pH. Based on these results I looked around to see what other specific types of mine drainage might be a good match, and the first thing that came to mind, was aluminum.

Test No.2—Could Zeolite help meet Aluminum Limits?

Over the last few years, aluminum limits have gotten so onerous that the last one I saw issued was for **(-0.5 mg/l)**. Well, it's not quite that bad, but pretty close and for a specific reason. The new lower aluminum limits would be tolerable but for having to report on a Total basis. What no one ("EPA") ever took into account was that the analytical methodology for aluminum is flawed. When you sample water and acidify the sample and digest the sample for analysis, you have just extracted aluminum that existed as part of the suspended solids (clays). As aluminum accounts for 8% of the earth's crust, you can have as little as 2-3 mg/l of suspended solids (our TSS limits are 35 mg/l) and exceed Trout stream limits of 0.08 mg/l. Consequently, the majority (my guess is 95%-99%) of so called aluminum exceedances for Non-AMD sites are not aluminum violations at all but merely the resultant of leaching aluminum from clay or some other soil type. What's the fix for this problem? Report aluminum on a Dissolved (filtered) basis for Non-AMD sites and you eliminate the false reporting currently taking place.

Now, for those sites which actually have Dissolved aluminum (not suspended solids type aluminum), there are essentially three categories to examine. **First**, there are those Non-AMD sites which have high quality-neutral pH water except that it contains Dissolved Aluminum concentrations of 0.10-0.20 mg/l with limits that range from 0.08 to

0.16 mg/l. The **Second** type includes those sites that are slightly acidic, contain minimal amounts of iron and manganese (meets limits without treatment), but contains as much as 5 mg/l of dissolved aluminum, with limits as low as 0.08 mg/l and up. The **Third** type, are those sites that treat AMD and resolubilize aluminum by way of treatment for manganese and/or ferrous iron, and have Aluminum limits as low as 0.08 mg/l and up. For this paper, the **First** and **Third** types were tested due to time constraints. However, based on results thus far, it may be said that the **Second** type water will respond as favorably as the others.

First Type---This particular water chemistry baffles me as it is alkaline water with Dissolved aluminum concentrations of as much as 0.20 mg/l. Based on the solubility curve of aluminum, this shouldn't occur but guess what—it does. For this particular type of water, the normal method of manipulating pH (whether up or down) to bring the dissolved aluminum out of solution does not work. Therefore, when you have this type situation and have been assigned extremely low aluminum limits such as 0.08 mg/l, panic and despair sets in rather quickly based on the possible treatment alternatives such as Reverse Osmosis—Distillation---etccc… I was able to obtain samples of this type of water in order to see if Zeolite could meet the demand of such a low limit as 0.08 mg/l.

The raw water quality for this part of the testing is as follows:

Parameter	Results
pH	7.03
Alkalinity	116.36
Acidity	<0.33
Dissolved Iron	0.10
Dissolved Manganese	0.26
Dissolved Aluminum	0.16

It's quite evident what most of you are thinking. You are saying to yourself that you wish you had such good quality and you wouldn't have to treat for aluminum and you would be right, unless you had a limit of 0.08 mg/l.

QUICK TIME OUT

I felt the need for a **Quick Time Out** to briefly explain to those reading this, that are not water chemistry freaks (or is that geeks), the reason I keep dealing with Dissolved concentrations when our N.P.D.E.S. limits are expressed as Total concentrations. The answer is quite simple and is based on a metal which is dissolved versus a metal which is in the solid form. In order to meet that Total limit in a conventional manner, the dissolved metals must be transformed into solid metals so they can precipitate (settle out), leaving the clarified water with a Total concentration (solid +dissolved=Total) less than the effluent limit. If after treatment, the Dissolved concentration is greater than the Total Limit, then settling is not applicable and that's when other more intrusive options such as Reverse Osmosis may come into play. Another way to look at Dissolved versus Total in regards to a discharge from an N.P.D.E.S. outlet is, if you check the outlet and you are exceeding your limits on a Total basis but meeting them on a Dissolved basis, then you have a physical problem. The pond may be full, water may be short circuiting, you might need baffles to increase retention time, etcccccc….. On the other hand, if you check your outlet and your Total limits are exceeded on a Dissolved basis, then you have a chemical problem and are not treating sufficiently to convert Dissolved to solid in order for precipitation (settling) to occur. Sorry for this **Time Out**, but it's amazing how the concept of Total versus Dissolved is so misunderstood by those who deal with treatment and the interpretation of the related analytical information. Hope this didn't add to the confusion and now, back to the test results.

As with the initial tests on the 3 samples of AMD, I kept it simple again and ran two tests of the alkaline water as previously described. The same size and amount of Zeolite was used and allowed contact for a couple of hours before analyzing.

Parameter	Raw Water	Zeolite-Test 1	Zeolite-Test 2
Dissolved Iron	**0.10**	**<0.01**	**<0.01**
Dissolved Manganese	**0.26**	**0.02**	**0.17**
Dissolved Aluminum	**0.16**	**0.03**	**0.04**

Once again, test results confirmed, Zeolite's extreme affinity for iron and aluminum, while also reducing the manganese concentration.

Third Type---OK, this is where things begin to get really interesting. This testing was performed on AMD treated for manganese removal at a high pH which resulted in resolubilization of just enough aluminum (the real kind of aluminum) to cause problems in meeting effluent limits. The obvious question was, how would the Zeolite react to this supercharged high pH water? Would it remove the resolubilized aluminum and what else might it do? Remember, although we haven't discussed it yet, Zeolite works on the basis of "**Cation Exchange**". That simply means, that when it takes in a cation such as aluminum, iron, manganese or some other cation, it then releases a cation or cations. Normally, those cations released are in the form of sodium and/or calcium. However, "**Watch Closely**" the exchange process when this over-treated water is exposed to the Zeolite. The reason I want you to "**Watch Closely**" is because the over-treated samples for this test, were over-treated using ***SODIUM*** hydroxide and ***CALCIUM*** hydroxide, both of which are normally released in the exchange process. Can you guess what happens and what the implications might be?

Parameter	Raw AMD	AMD-NaOH	AMD-NaOH Zeolite	AMD-Ca(OH)2	AMD-Ca(OH)2 Zeolite
pH	**3.45**	**10.89**	**8.29**	**11.71**	**9.64**
Alkalinity	**<0.45**	**162.64**	**25.23**	**604.67**	**31.51**
Acidity	**739.89**	**<0.33**	**<0.33**	**<0.33**	**<0.33**
Conductivity	**4,410.00**	**4,310.00**	**2,548.00**	**4,820.00**	**2,677.00**
Dissolved Fe	**213.00**	**0.01**	**0.04**	**0.02**	**0.01**
Dissolved Mn	**30.50**	**<0.001**	**0.02**	**0.001**	**<0.001**
Dissolved Al	**52.68**	**1.46**	**<0.008**	**0.127**	**<0.008**
Dissolved Na	**25.78**	***871.30***	***336.20***	***54.44***	***156.80***
Dissolved Mg	**149.30**	**0.34**	**35.37**	**0.24**	**16.01**
Dissolved Ca	**194.86**	***84.61***	***221.60***	***936.30***	***518.40***
TDS	**3,111.00**	**2,914.00**	**2,025.00**	**3,320.00**	**2,120.00**

I know I have said this before, but **WOW!!!!!!** There is an entirely separate paper here just on these results. Before you waste a lot of time trying to balance the different constituents, please note that I left out some analysis, one of which is sulfates. The results as presented, offer more than enough to chew on for a while until further work can be done in relation to sulfates and chlorides. Also, this test is where Zeolite picks up the **BA** part of **MBBAR.** It is now officially one **Mind Blowing Bad Ass Rock**.

Just in case you need a little guidance with understanding the chart, see below:

--The first column list the parameters analyzed.
--The second column, Raw AMD, is the test water analyzed before treatment.
--The third column, AMD-NaOH, are the results of treating the AMD with 20% Sodium Hydroxide.
--The fourth column, AMD-NaOH/Zeolite, illustrates the results from taking the clarified effluent from the third column and allowing it to contact the Zeolite for 1.5 hours.
--The fifth column, AMD-Ca(OH)2, contains the results of treating the AMD with hydrate lime.
--The sixth column, AMD-Ca(OH)2/Zeolite, illustrates the results from taking the clarified effluent from the fifth column and allowing it to contact the Zeolite for 1.5 hours.

As I said, I could write another paper and spend a lot of time on just these results, along with the ones left out. However, let me just point out some of the highlights, as we still have more test results to cover.

1—The pH of 10.89 for 20% NaOH treated AMD and the 11.71 pH for the Ca(OH)2 treated AMD, would take 2-4 days for the pH to drop to the levels recorded by 1.5 hours of Zeolite contact. Why?
2—The conductivity for both post Zeolite treated effluents was reduced substantially.
3—The resolubilized aluminum for both treated AMD samples was reduced to <0.008 mg/l. This proved that the complex chemistry of the over-treated water did not affect the cation exchange properties regarding aluminum.
4—The Zeolite actually removed over 500 mg/l of sodium from the effluent where the AMD was treated with 20% sodium hydroxide.
5-- The Zeolite actually removed over 400 mg/l of calcium from the effluent where the AMD was treated with hydrate lime.
6—As per conductivity, the Total Dissolved Solids was reduced post contact with Zeolite.

As stated, the test was conclusive in regards to removing the resolubilized aluminum, but the overall results led me into a completely different direction for the use of Zeolite for conventionally treated mine drainage. Although we have proven that the Zeolite removes metals from raw AMD as a primary remediation system, what if we now consider what remediation benefits it might offer to water already treated by sodium hydroxide or hydrate/calcium oxide and is now ready for discharge. I know----now you know that I am truly certifiable for suggesting that you might want to run the treated water that now meets iron/manganese, and maybe aluminum , through Zeolite prior to the final discharge. The obvious and eye popping revelation from this test, revolves around Dissolved Solids and in Pennsylvania, Osmotic Pressure. Over the past 5-10 years there has been a significant effort to make Dissolved Solids/Conductivity a specific limit in mine drainage N.P.D.E.S. permits. However, as anyone in the business recognizes, removal of the Dissolved Solids after conventional treatment, is tied to removal of Sulfates, Chlorides, and guess what??? Sodium-Calcium-Magnesium. To remove such type parameters generally (99% of the time) poses an insurmountable financial hurdle to most coal operators. Only those, who will remain nameless, that spend $150,000,000 to provide a system that through RO-Distillation, and other exotic methods, can achieve such removal. Pennsylvania has moved ahead with their offering of a Dissolved Solid limit through the assignment of an Osmotic Pressure limit. I know, it's almost like my reaction to Zeolite—Zeo What? Os What? As I normally do in these modern times, when first hearing this term while working on a project in Pennsylvania, I "Googled" it and ended up in Wikipedia again. Below is the definition I found.

Osmotic pressure[edit]

Main article: Osmotic pressure

As mentioned before, osmosis may be opposed by increasing the pressure in the region of high solute concentration with respect to that in the low solute concentration region. The force per unit area, or pressure, required to prevent the passage of water through a selectively permeable membrane and into a solution of greater concentration is equivalent to the osmotic pressure of the solution, or turgor. Osmotic pressure is a colligative property, meaning that the property depends on the concentration of the solute, but not on its identity. It also is involved in facilitated diffusion.

After much introspection and meditation about this definition, I resolved that it meant if the dissolved solids were too high, then the "bugs" couldn't poop. Consequently, to minimize this stressful situation, Pennsylvania is issuing OP limits which, if I understand correctly, are being done so as N.P.D.E.S. permits come up for renewal. To further understand OP, I contacted Bill Allen of the PADEP (great guy), and he was kind enough to send me information that contained two methods by which to project OP from water analysis itself and information concerning a laboratory test for OP. The most complete method from an analytical perspective-short of an actual lab tests is demonstrated by the following formula.

OP = .0104 X Sulfate + .0282 X Chloride + .0434 X Sodium + .0412 X Magnesium + .0249 X Calcium + .0256 X Potassium + .0164 X Bi-carbonate

It is evident from the formula, that sodium, magnesium, and calcium play a major role with respect to the final OP value. So, if you were trying to reduce the OP, one would focus on the dissolved solids that provided the "biggest bang for the buck". As I did not sample for all of the parameters above, there is a more benign (obviously not as accurate) method by which you can get an idea of OP. The formula for this is,

$$OP = TDS/34$$

Of the permits I have seen with OP limits thus far, the number may vary but an average value might be close to 50. With that in mind, look at the analysis of the raw and treated water from this test as it applies to TDS/34.

Raw AMD TDS = 3,110 = 3,110/34 = an OP of **91.47**

Sodium Hydroxide treated AMD TDS = 2,914/34 = an OP of **85.70**
Sodium Hydroxide treated after Zeolite TDS = 2,025/34 = an OP of **59.55**

Hydrate Lime treated AMD TDS = 3,320/34 = an OP of **97.64**
Hydrate Lime treated after Zeolite TDS = 2,120/34 = an OP of **62.35**

Time for another WOW!!!!! Yes, it's true that it wasn't reduced to 50, but look at the substantial reduction offered by the Zeolite from removing sodium in sodium hydroxide treated water, and from removing calcium in hydrate lime/calcium oxide treated water. If the other parameters necessary to run the more extended formula had been tested, the OP should have been below 50, based on other water analysis that I have previously worked with.

So far, we have learned that Zeolite will remove a variety of metals, it will raise low pH values up to circum-neutral, it will reduce high pH values from over-treatment for manganese, and now, we have determined that it can reduce dissolved solids from conventionally treated mine drainage.

Questions that remain to be answered are,
--How much contact time is required for Zeolite to **"Do Its' Thing"**?
--How long can you use Zeolite before it "**Fills Up**"?
--Is there a way to **"Re-Use"** Zeolite once it "Fills Up"?

Test No.3—How much Contact Time is Required?

To carry out this test, I chose Alkaline Manganese water purposely, since Zeolite has a more casual relationship with that metal versus its love for iron and aluminum. The Raw water analysis for this test was,

Parameter	Analysis
pH	**6.74**
Alkalinity	**71.91**
Dissolved Iron	**<0.01**
Dissolved Manganese	**2.65**
Dissolved Aluminum	**0.014**
Dissolved Sodium	**2.99**
Dissolved Magnesium	**30.10**
Dissolved Calcium	**51.25**

Since there was no iron or aluminum present in the water, manganese, sodium, magnesium, and calcium were chosen as the parameters of interest for this test. As this is a selective cation exchange process, it would be beneficial to learn more about what goes in and what comes out. The test consisted of running 10 sets of 450 ml's of Raw water samples through the same Zeolite for specific increments of time. Those increments were as follows:

No.1—Raw water was in contact with Zeolite for 1 minute.
No.2—Raw water was in contact with Zeolite for 2 minutes.
No.3—Raw water was in contact with Zeolite for 3 minutes.
No.10—Raw water was in contact with Zeolite for 10 minutes.

Parameter	Raw	1 Min.	2 Min.	3 Min.	4 Min.	5 Min.	6 Min.	7 Min.	8 Min.	9 Min.	10 Min.
Diss. Mn	**2.65**	**1.948**	**1.99**	**2.02**	**2.01**	**1.97**	**2.11**	**1.97**	**1.96**	**2.01**	**1.97**
Diss. Na	**2.99**	**15.98**	**17.06**	**17.08**	**18.17**	**18.66**	**16.54**	**48.99**	**18.95**	**18.15**	**34.65**
Diss. Mg	**30.10**	**23.02**	**24.11**	**24.89**	**24.62**	**24.58**	**25.79**	**25.17**	**24.71**	**25.21**	**25.19**
Diss. Ca	**51.25**	**51.90**	**55.49**	**57.67**	**58.11**	**59.85**	**60.08**	**62.01**	**60.48**	**61.13**	**61.42**

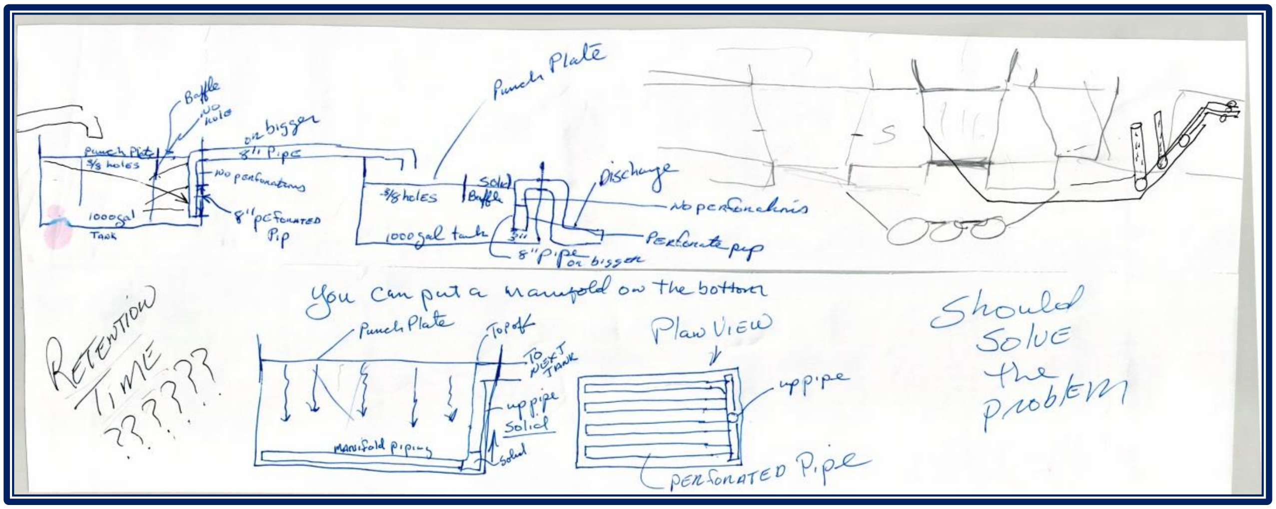
The goal for manganese removal in this series of tests was to meet an effluent limit of 2 mg/l. I had no idea what the actual results would be, but was delighted to find out that a minimal contact time of 1 minute would essentially meet that limit for this particular water. Obviously, every water would be different based on a number of variables and would need to be tested to determine the proper amount of contact time to achieve the assigned limit. Note, that there was almost an equilibrium condition established in regards to the exchange of Manganese/Magnesium for Sodium/Calcium. Unlike the previous test, where sodium and calcium were taken in, in this test, they were expelled from the Zeolite.

The limited testing performed thus far has taught me not to try to anticipate how the Cation exchange process will occur. It appears that the specific chemistry of each application will determine who is booted out and who is allowed in…..

Test No.4—How long before Zeolite fills up?

Based on results from the previous tests, it's looking more and more as if determining how much loading it takes to "Fill-Up" the Zeolite will be difficult to predict, since it depends on the specific water chemistry and since, the water chemistry is so variable from site to site. That doesn't mean it can't be done, but it would seem that to devise a credible methodology for making such a prediction, would require a number of actual field applications covering as many different types of mine drainage qualities as possible. Actual field testing would be preferable to laboratory testing to account for the other related inefficiencies that plague any system that requires contact time with a specific medium. It's sort of like comparing a lab titration test using hydrate lime to what is actually going to happen out in the field. The lab titration test essentially attains a near 100% solubilization of the lime, whereas the actual field application may achieve as little as 50%-60% efficiency. I realize that I am crossing the line with respect to the chemical versus physical aspects of treatment, but both combined do constitute the whole of treatment when designing a system and projecting treatment costs.

As a short side note, the Zeolite will encounter the same efficiency problems as with limestone beds and vertical flow ponds and that is, distribution of flow to maximize contact time. Any of you that have done work with Passive systems utilizing limestone beds, fully understands that water will channel through the beds simply due to the variability of the bed density. Over time, these channels will further develop specific flow paths and drastically reduce the overall contact time with the treatment medium in the bed. One of my favorite examples of this was two sets of parallel limestone beds where each was designed to have 24 hours retention/contact time. As 35 years of water treatment type work has taught me, “Murphy’s Law” and the “ASSUME” theorem applies 99% of the time in this line of work, so you had best not leave anything to chance. Consequently, dye tracing is a mandatory aspect of treatment system testing whether for determining contact time in a passive system or determining retention time in a settling pond after chemical treatment. Anyway, after the two limestone beds were completed and water had been allowed to run long enough to achieve an equilibrium condition, dye was introduced into the feed points of the ditches. We gathered up our stuff laying around the beds and planned to go to another site and then come back later in the day just to check and make sure that the dye hadn’t made it through the beds. Long story short—the dye made it through the beds before we got to our truck. There was a total of less than 30 minutes of contact time for each bed. Wow!!!! That’s not exactly what we said but you get the idea. So, it would only seem logical to include not only projections of the Zeolite capacity based on loading, but to also account for contact time since it would determine the volume of material required. To that extent, my dedicated assistant “J. Campbell”, spent days, or was that hours, or a few minutes on a whiteboard, developing <u>complex detailed design drawings</u> as seen below, to maximize retention time.



A picture is worth a thousand words isn’t it??????

It wasn’t my intention to get sidetracked again, but this type of treatment system only works based on “Distribution of Flow”-“Distribution of Flow”-Distribution of Flow”, which directly relates to “Retention Time”-“Retention Time”-“Retention Time”.

Now, back to trying to determine if there is a way to project Zeolite capacity based on loading. In attempting to accomplish this through testing, the alkaline manganese water was used for this test. The test consisted of running 25 sets of 450 ml’s of Raw water samples through the same 2.5 lbs. (amount in a 1,000 ml cylinder as previously illustrated) of zeolite over varying periods of time. Contact time was varied to see how much of a difference it actually made in regards to the exchange of the targeted Cations, based on the results we got from **Test No.3**.

25 Repetitions of 450 ml of Raw Alkaline Mn Water in 2.152 lBs. 1/2”X1/4” Zeolite @ Var. Time Increments

Sample	Time	Raw Mn	Zeo-Mn	Net Mn	Raw Na	Zeo-Na	Raw Mg	Zeo-Mg	Raw Ca	Zeo-Ca
1	30 Min.	2.65	0.73	-1.92	2.99	24.55	30.10	18.91	51.25	67.09
2	30 Min.	2.65	0.97	-1.68	2.99	19.54	30.10	20.18	51.25	63.95
3	60 Min.	2.65	0.72	-1.93	2.99	23.55	30.10	19.00	51.25	66.99
4	30 Min.	2.65	1.07	-1.58	2.99	17.06	30.10	20.81	51.25	62.67
5	60 Min.	2.65	0.97	-1.68	2.99	19.12	30.10	20.55	51.25	63.56
6	45 Min.	2.65	1.08	-1.57	2.99	17.42	30.10	21.23	51.25	62.46
7	60 Min.	2.65	0.99	-1.66	2.99	18.56	30.10	20.10	51.25	61.70
8	90 Min.	2.65	0.99	-1.66	2.99	18.97	30.10	20.49	51.25	62.28
9	18 Hrs.	2.65	0.58	-2.07	2.99	32.05	30.10	20.65	51.25	76.59
10	60 Min.	2.65	0.88	-1.77	2.99	21.34	30.10	20.57	51.25	64.48
11	60 Min.	2.65	1.03	-1.62	2.99	18.74	30.10	21.29	51.25	63.61
12	60 Min.	2.65	1.12	-1.53	2.99	17.39	30.10	21.88	51.25	63.33
13	60 Min.	2.65	1.19	-1.46	2.99	16.09	30.10	21.96	51.25	62.22
14	90 Min.	2.65	1.16	-1.49	2.99	17.04	30.10	22.02	51.25	63.12
15	15 Hrs.	2.65	0.82	-1.83	2.99	25.42	30.10	21.17	51.25	68.74
16	60 Min.	2.65	1.06	-1.59	2.99	17.43	30.10	21.19	51.25	60.51
17	90 Min.	2.65	1.16	-1.49	2.99	17.73	30.10	22.27	51.25	62.67
18	60 Min.	2.65	1.28	-1.37	2.99	15.05	30.10	22.43	51.25	60.37
19	90 Min.	2.65	1.30	-1.35	2.99	15.06	30.10	22.51	51.25	61.11
20	90 Min.	2.65	1.34	-1.31	2.99	14.94	30.10	22.92	51.25	60.67
21	120 Min.	2.65	1.08	-1.57	2.99	23.36	30.10	23.41	51.25	67.09
22	24 Hrs.	2.65	0.94	-1.71	2.99	28.71	30.10	24.23	51.25	86.29
23	100 Min.	2.65	1.21	-1.44	2.99	20.14	30.10	23.32	51.25	75.97
24	90 Min.	2.65	1.31	-1.34	2.99	17.89	30.10	23.43	51.25	72.99
25	120 Min.	2.65	1.35	-1.30	2.99	16.10	30.10	23.32	51.25	70.71

The results once again illustrated an equilibrium condition that was established between the subject Cations. As before, the target was an effluent limit of 2 mg/l, which was easily met over the 25 repetitions, and even though the amount of manganese being removed was diminishing as testing proceeded, it was still far below that 2 mg/l limit, at 1.35 mg/l after repetition No.25. After three days of testing, it was obvious that a continuous column leachate test should have been performed, but rather than to start over, the attempt to determine capacity based on loading is relegated to future field tests to be conducted in the near future.

With that decided, there was another aspect of Zeolite which had to be investigated, and that was to see if the Zeolite could be **"Re-Used"** once it reached its initial Cation Exchange Capacity.

Test No.5—Is there a Way to "Re-Use" Zeolite?

Currently, Zeolite costs about +/- $200/ton to have delivered here in the Appalachians. It seemed intuitive that if the Zeolite had to be replaced when the CEC had been reached, that in itself, would limit the number and diversity of mine drainage treatment applications. After wading through some more technical papers, there was mention of a process to "**Renew**" Zeolite by exposing the spent rock to a 2% saline solution (NaCl-salt). A salt solution was mixed up from some Morton salt in the kitchen (have no idea what % solution, but was much higher than 2 %), and made ready for the "Renewal" testing. Even though I never completed loading the Zeolite from the previous 25 repetitions testing, the Zeolite used for this testing was chosen to at least get an idea, if what went in- would be cast out by the saline solution. In addition to the "Renewal" testing itself, another 10 repetitions of the alkaline manganese water was run through the now "Renewed" Zeolite to see how it would react. Review the results of the testing on the following before discussing further.

25 Repetitions of 450 ml of Raw Alkaline Mn Water 1/2"X1/4" Zeolite Followed by 6 Repetitions of Saline Solution Through Same Zeolite & Then Another 10 Repetitions of Alkaline Mn Water

Sample	Time	Raw Mn	Zeo-Mn	Net Mn	Raw Na	Zeo-Na	Raw Mg	Zeo-Mg	Raw Ca	Zeo-Ca
1	30 Min.	2.65	0.73	-1.92	2.99	24.55	30.10	18.91	51.25	67.09
2	30 Min.	2.65	0.97	-1.68	2.99	19.54	30.10	20.18	51.25	63.95
3	60 Min.	2.65	0.72	-1.93	2.99	23.55	30.10	19.00	51.25	66.99
4	30 Min.	2.65	1.07	-1.58	2.99	17.06	30.10	20.81	51.25	62.67
5	60 Min.	2.65	0.97	-1.68	2.99	19.12	30.10	20.55	51.25	63.56
6	45 Min.	2.65	1.08	-1.57	2.99	17.42	30.10	21.23	51.25	62.46
7	60 Min.	2.65	0.99	-1.66	2.99	18.56	30.10	20.10	51.25	61.70
8	90 Min.	2.65	0.99	-1.66	2.99	18.97	30.10	20.49	51.25	62.28
9	18 Hrs.	2.65	0.58	-2.07	2.99	32.05	30.10	20.65	51.25	76.59
10	60 Min.	2.65	0.88	-1.77	2.99	21.34	30.10	20.57	51.25	64.48
11	60 Min.	2.65	1.03	-1.62	2.99	18.74	30.10	21.29	51.25	63.61
12	60 Min.	2.65	1.12	-1.53	2.99	17.39	30.10	21.88	51.25	63.33
13	60 Min.	2.65	1.19	-1.46	2.99	16.09	30.10	21.96	51.25	62.22
14	90 Min.	2.65	1.16	-1.49	2.99	17.04	30.10	22.02	51.25	63.12
15	15 Hrs.	2.65	0.82	-1.83	2.99	25.42	30.10	21.17	51.25	68.74
16	60 Min.	2.65	1.06	-1.59	2.99	17.43	30.10	21.19	51.25	60.51
17	90 Min.	2.65	1.16	-1.49	2.99	17.73	30.10	22.27	51.25	62.67
18	60 Min.	2.65	1.28	-1.37	2.99	15.05	30.10	22.43	51.25	60.37
19	90 Min.	2.65	1.30	-1.35	2.99	15.06	30.10	22.51	51.25	61.11
20	90 Min.	2.65	1.34	-1.31	2.99	14.94	30.10	22.92	51.25	60.67
21	120 Min.	2.65	1.08	-1.57	2.99	23.36	30.10	23.41	51.25	67.09
22	24 Hrs.	2.65	0.94	-1.71	2.99	28.71	30.10	24.23	51.25	86.29
23	100 Min.	2.65	1.21	-1.44	2.99	20.14	30.10	23.32	51.25	75.97
24	90 Min.	2.65	1.31	-1.34	2.99	17.89	30.10	23.43	51.25	72.99
25	120 Min.	2.65	1.35	-1.30	2.99	16.10	30.10	23.32	51.25	70.71
Saline 1	16 Hrs.		22.65			13,491		551.85		4,420.50
Saline 2	48 Hrs.		10.65			21,750		362.70		4,198.50
Saline 3	60 Min.		3.00			26,100		106.50		1,414.05
Saline 4	120 Min.		1.65			27,315		55.80		791.55
Saline 5	24 Hrs.		2.55			25,485		280.65		3,865.54
Saline 6	18 Hrs.		8.90			17,880		203.45		1,432.00
26	30 Min.	2.56	*0.93*	*-1.63*	2.21	*2,984*	29.77	*31.50*	55.52	*277.20*
27	45 Min.	2.56	*0.75*	*-1.81*	2.21	*1,982*	29.77	*19.49*	55.52	*127.70*
28	45 Min.	2.56	*0.56*	*-2.00*	2.21	*1,182*	29.77	*11.42*	55.52	*55.91*
29	30 Min.	2.56	*0.47*	*-2.09*	2.21	*673*	29.77	*7.90*	55.52	*27.51*
30	30 Min.	2.56	*0.41*	*-2.15*	2.21	*497*	29.77	*6.32*	55.52	*18.23*
31	30 Min.	2.56	*0.27*	*-2.29*	2.21	*491*	29.77	*4.27*	55.52	*12.14*
32	30 Min.	2.56	*0.29*	*-2.27*	2.21	*310*	29.77	*4.42*	55.52	*9.97*
33	30 Min.	2.56	*0.31*	*-2.25*	2.21	*248.50*	29.77	*4.24*	55.52	*8.09*
34	30 Min.	2.56	*0.28*	*-2.28*	2.21	*197.80*	29.77	*3.94*	55.52	*6.99*
35	30 Min.	2.56	*0.34*	*-2.22*	2.21	*170.30*	29.77	*4.49*	55.52	*7.69*

Manganese test results of the initial 25 Repetitions, indicates that based on the assumption that a volume of 450 ml was used for each repetition, 17.96 mg of manganese was extracted by the Zeolite. Using the same analogy from the 6 Saline Solution

Repetitions, 22.23 mg of Mn was released back to the water. Pretty close, considering I wasn't very precise with regards to the 450 ml for each Repetition. So, it looks like that what went in, did in fact come back out. Probably as much of a surprise or more, with regards to the overall test results, were the magnesium and calcium concentrations that were expelled from the Zeolite. To illustrate this, note the raw water quality of the saline solution versus the Mg and Ca that came out.

Saline Solution Quality

pH	**6.14**
Fe (mg/l)	**0.03**
Mn (mg/l)	**0.04**
Al (mg/l)	**0.01**
Na (mg/l)	**28,050**
Mg (mg/l)	**1.34**
Ca (mg/l)	**27.45**

Raw Mg (mg/l)	Expelled Mg (mg/l)	Raw Ca (mg/l)	Expelled Ca (mg/l)
1.34	551.85	27.45	4,420.50
1.34	362.70	27.45	4,198.50
1.34	106.50	27.45	1,414.05
1.34	55.80	27.45	791.55
1.34	280.65	27.45	3,865.54
1.34	203.45	27.45	1,432.00

These results definitely illustrates that there is much-much more to Zeolite than meets the eye. Why were so much of the Mg and Ca expelled from the Zeolite? It was obviously due to my slightly higher than 2% salt solution. The question is, would we want to actually achieve such high concentrations of Mg and Ca expelled during the Renewal process? To shed some light on this question, observe the results of the 10 Alkaline Manganese water repetitions after the Saline Solution Renewal. ***It should be noted that there is a very slight difference in the raw water analysis of the final 10 Repetitions. This was due to the fact that I had finally depleted my original sample of Alkaline Mn water and had to return to the same source for more. However, as seen, this source is quite consistent with regards to quality and did not affect the final test results.***

Alkaline Mn water Repetitions Post NaCl Renewal Process

Raw Mg (mg/l)	Zeo Mg (mg/l)	Raw Ca (mg/l)	Zeo Ca (mg/l)
29.77	*31.50*	55.52	*277.20*
29.77	*19.49*	55.52	*127.70*
29.77	*11.42*	55.52	*55.91*
29.77	*7.90*	55.52	*27.51*
29.77	*6.32*	55.52	*18.23*
29.77	*4.27*	55.52	*12.14*
29.77	*4.42*	55.52	*9.97*
29.77	*4.24*	55.52	*8.09*
29.77	*3.94*	55.52	*6.99*
29.77	*4.49*	55.52	*7.69*

To understand these results, you will need to look back at the original 25 Repetitions for comparison. In doing so, it will become obvious that after the Saline Solution Renewal, the Zeolite recovered more magnesium than from the initial 25 repetitions and the calcium, instead of being expelled from the Zeolite, reversed the reaction to recover it. These test results again showcase the complex nature of Zeolite chemistry but at the same time, offers a look at how the Zeolite itself may be transformed to perform in a specific manner based on the particular treatment needs of a site. As seen in previous testing, Zeolite can be used to treat-treated water to reduce dissolved solids-AKA Osmotic Pressure. What if you "Renewed" the Zeolite before using it to treat hydrate lime treated water? Imagine how much calcium would be removed in the effort to reduce OP and/or Dissolved Solids?

Another tidbit of related information from the final 10 Repetitions, involved the removal of additional manganese versus the initial 25 Repetitions. Like magnesium and calcium, the Saline Solution Renewal enhanced the ability of the Zeolite to accept more manganese over the same contact time. Are all of these Renewal results telling us that you might want to consider renewing the Zeolite ahead of any type of treatment to increase its' overall removal efficiency? The answer to that is, it probably depends. The Renewal test results themselves, have left me wondering if other specific solutions besides sodium chloride, might be used to enhance removal of a specific cation.

One final observation with regards to the Renewal tests concerns the amount of sodium released back into the Alkaline Manganese water. This is not something that would be acceptable but there may have been an understandable reason for such large concentrations being released. First, I'm not sure what % solution I made, but when I dropped my metal mixing spoon in the saline solution mixture, it floated—that can't be a good thing, can it? Also, it may be noted that the sodium concentration rapidly decreased from 1,982 mg/l in the first of the final 10 Repetitions to 170.30 mg/l in the No.10 Repetition. Therefore, had I used the appropriate 5 saline solution, it would seem logical that the released sodium concentrations would have been much reduced. There are even thoughts, that prior to using a Saline Solution Renewed Zeolite, that you rinse it with water prior to putting it back on-line for treatment. Anyway, for those who would have looked at the charts close enough to detect this anomaly, "that's my story and I'm sticking to it".

I know that you are as worn out trying to finish reading this as I am in trying to finish writing it, so I am concluding **Chapter 1—Introduction to the Use of Zeolite in the Treatment of Raw/Treated Mine Drainage**, and will return at some point in the future with **Chapter 2-Actual Field Trials and Results of Using Zeolite**. With that said, let me have your attention for just a couple more minutes to summarize what we have learned from the initial lab testing.

SUMMARY REMARKS

The question that you most want to ask is, how much will it cost to treat your own particular water with Zeolite? I would most certainly like to answer that question, but that will remain unknown to both of us until sufficient field trials have been conducted to resolve all the issues revealed in this report. Zeolite possesses a number of treatment capabilities that are unrivaled with respect to nearly any other form of mine drainage remediation and offers resolution of numerous issues that before now have seemed unresolvable by a conventional and affordable treatment methodology. Do I think that Zeolite is that "Magic Pill" that we have so desperately been looking for over the past 30 years? No, but it does hold the potential to offer an alternative in site specific situations and will be added as a multi-purpose tool to our mine drainage tool box. I would recommend and encourage you, that if you have any of the issues that have been discussed in this report, or for that matter, any chemistry related mine drainage treatment problems, take an in depth look at Zeolite and do some testing yourself. However, in doing so, "a word of caution about Zeolites: All zeolites are not created equal. Zeolite is a generic mineral classification and there are over 40 different types of natural zeolite. Even zeolites within the same category vary from deposit to deposit in chemistry and physical properties and you shouldn't expect the zeolite from Source B to replicate the results obtained from Source A. The findings presented here are from the clinoptilolite zeolite produced by St. Cloud Mining Company at its Winston, NM deposit."

In closing this Chapter, let's take one more look at the treatment capabilities discovered from this initial testing.

--**Zeolite** will raise low pH by extracting the Hydrogen Ions associated with such.
--**Zeolite** reduces pH from over-treatment for Manganese. (Don't yet know why.)
--**Zeolite** removes Dissolved Iron.
--**Zeolite** removes Dissolved Aluminum.
--**Zeolite** removes Dissolved Manganese.
--**Zeolite** removes resolubilized aluminum due to high pH.
--**Zeolite** reduces Dissolved Solids by removing Na or Ca from conventionally treated mine drainage.
--**Zeolite** can be renewed once the CEC, Cation Exchange Capacity has been reached through the use of a saline solution.
--A Saline Solution Renewal process may be preferable, prior to using for treatment to enhance extraction ratios by expelling other cations inherent to the **Zeolite** structure itself.
--**Zeolite** does not produce a solid sludge, but rather releases all the treatment related extracted metals in a dissolved form during the renewal process. This solution may then be collected and hauled to a disposal site such as the local sewage plant or to a lined evaporation cell near the site.
--**Zeolite** probably has many other potential treatment capabilities which have yet to be revealed.

Is Zeolite applicable for your situation?
<u>TO BE DETERMINED</u>

Physicochemical and microbiological mechanisms of metals removal during passive mine water treatment at low and circumneutral pH

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Abstract

Results from two studies on the treatment of low pH metal mine water and circumneutral coal mine water are presented. These involve using vertical flow mine water treatment systems where mine water is directed through a unreactive gravel bed to encourage metal removal under aerobic conditions. This study highlight previously under-reported physicochemical and microbiological mechanisms responsible for the removal of iron at low pH, and manganese and trace metals at circumneutral pH. These mechanisms can be harnessed for the passive treatment of acidic and circumneutral mine water and have implications for the biogeochemistry of mine sites and transport of metals in the environment. At the low pH site (~pH 2.9), significant removal of iron, as high as (85%) was shown in vertical flow system, the mechanism is thought to be removal predominantly by the crystal growth and/or aggregation and filtration of nanoparticulate Fe(III). Centrifugation indicates that $Fe(III)_{(s)}$ present are < 35nm. Also microbial Fe(II) oxidation and bioprecipitation of Fe(IIII) is important at times. The circumneutral site data shows manganese removal at high rates can be achieved by contacting iron and manganese bearing mine water with an accreting bed of ochre. The vertical flow of Fe(II) and Mn(II) -bearing water through an accreting bed leads to spontaneous formation of Fe/Mn banding structures in the ochre bed and also leads to the removal of other contaminants of concern notably thallium and cobolt, with ochre from the vertical flow system being demonstrably enriched in these elements compared to settling lagoon ochre from the same site. The use of vertical flow reactors represent an attractive option for (i) the removal of iron from low pH mine water without the requirement for any pH adjustment, and (ii) removal of iron and manganese and trace metals from circumneutral mine water.

Solving Mine Water Problems with Peat-based Sorption Media

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Mine water often contains elevated levels of trace metals that must be removed prior to discharge. Conventional technologies exist but generally are labor intensive and expensive. Peat-based sorption material can be a less expensive alternative and is easily deployed in either "semi-active" or passive treatment designs. APTsorb^{TM}, a hardened granular material produced by American Peat Technologies from natural reed sedge peat, is a uniform material with a hydraulic conductivity of around 1 cm/sec, and metal removal capacity ranging from 1 -15% on a dry weight basis. It has been used successfully to remove suspended and dissolved copper from the Soudan iron mine in Minnesota and suspended and dissolved Pb, Zn and Cd from a lead mine in North America.

Since 2009, water discharging from the Soudan mine has been treated with a commercial ion exchange resin system that includes flow equalization tanks, bag and cartridge filters, a break tank, a carbon tank and several ion exchange tanks. Although effective, the system's high cost, inefficient removal of suspended material and substantial maintenance have been ongoing and troublesome issues.

In November 2012, a pilot test was initiated using a single tank of APTsorb^{TM}. Mine water was pumped through the media without any pretreatment. Copper input typically ranges from 30 – 60 ug/l but concentrations increased to a maximum value of around 300 ug/l in the summer of 2013. Since startup, over 16.5 million gallons (> 32,000 bed volumes) have been treated with an average removal of around 75% for suspended copper and 60% for dissolved copper. Backwash is required at about 4000 bed volumes, but with a combination of air sparging and high flow backwash, the suspended material is effectively removed from the bed.

The APTsorb media produced equivalent copper removal to the existing treatment system components of the bag and cartridge filters, the break tank, the carbon tank and the first commercial ion exchange tank. By reducing the size and complexity of the system, the capital and operation and maintenance costs are substantially reduced. Based on the existing data, using a single APTsorb tank will reduce annual operating costs by about a factor of 6; from around $130,000 to $21,000.

A pilot test was initiated at a lead mine in North America in October 2013. The pilot was designed to model both a "semi-active" (pressurized tank) and passive (biocell) treatment system approach. The original plan was to treat the discharge from the clarification basin, but if the mine discharge could be treated directly, the basin could be eliminated. To accommodate this approach, a pressurized sand filter was installed before both systems.

Input mine water had a pH greater than 7 and contained about 1500 ug/l total lead, with about 90% in the suspended form. Total metals concentration varied with the amount of total suspended solids in the discharge. The sand filter essentially removed all suspended metals, but removal did decrease as the pressure drop over the filter increased. Lead removal in both pilot systems was generally greater than 99%. Excessive solids in the mine discharge contaminated the pressurized tank and affected treatment at 6400 bed volumes. This reduced dissolved metal removal efficiency in the media from 99% to about 85%

and caused the discharge to exceed the permit limit of 11 ug/l lead. The biocell was not affected and discharge limits are still being met after 12000 bed volumes.

US Peroxide
Technologies for a clean environment

US Peroxide is the leading supplier of hydrogen peroxide-based technologies and services for environmental applications. We have been serving the water, wastewater and remediation markets for over 20 years and have offices and field service locations throughout North America.

Acid Mine Drainage Programs Include These Services:

1. Full-service, “hands off” solutions
2. Chemical supply
3. Application expertise
4. Storage and dosing systems
5. Inventory and logistics management
6. Ongoing field and technical support

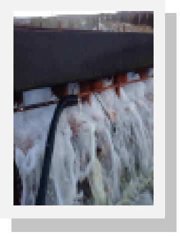
Turn-key Program Benefits

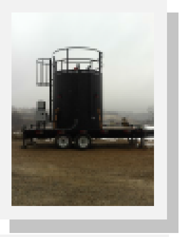
- Reduced Chemical Costs
- Less Solids for Disposal
- Energy Cost Savings

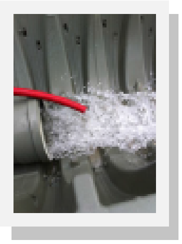
Our consultative approach to problem solving includes application assessment, technology selection (which may include lab scale testing, if necessary) and development of a tailored treatment approach. Our turn-key programs successfully integrate storage and dosing equipment systems, chemical supply, inventory and logistics management, and ongoing field and technical support. This approach provides cost-effective “hands-off” solutions to our customers.

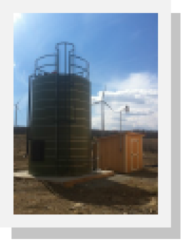
W.K. MERRIMAN, INC.
Chemical & Environmental Technology

MINE WATER TREATMENT









WKM specializes in value-added water treatment technology and commodity chemicals. Our service program includes system surveys, equipment recommendations, and utilization of green products and non-hazardous slurries. With the combination of Fortune 500 producers and our experienced team, we provide quality products and creative technical expertise.

SERVICES

Cost-Benefit Analysis

Equipment & Trail Conversions

24-Hour Availability for Orders

Lab Testing & Analysis

Customer Inventory Monitoring

Creative Technical Expertise

PRIMARY PRODUCTS

Lime Slurry

Hydrated Lime

Caustic Soda

W.K. Merriman Inc.

W.K. Merriman, Inc. was established in 1986. At a time when major chemical producers were looking at personnel cutbacks, W.K. Merriman, Inc. has grown to meet the daily service requirements of our customers, and the goals of our suppliers. Over the years, we have developed a business relationship with a number of producers, and are continuously on the lookout for new products and suppliers to best fit our coal customer's needs.

W.K. Merriman, Inc.
Chemical and Environmental Technology

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Phone: 412-262-7024
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www.wkmerriman.com

Certified WBENC Women's Business Enterprise

National WBE Certification #253342

KROFF
Mining and Aggregates
www.kroff.com

Program Benefits
Kroff Chemical Company, Inc. provides you with on-site technical expertise from experienced field personnel. Our consultants bring extensive experience to solving your mine drainage concerns. With our team of mining and aggregates experts combining over 50 years of experience, we can ensure that you have the most effective treatment strategy possible.

Achieve and Maintain Outlet Compliance
Environmental regulations are ever-changing. What may be in compliance today, may not be in compliance tomorrow. Your Kroff consultant will work with you to design a treatment program, using a combination of mechanical and chemical approaches to ensure your outlet discharges meet all current regulations.

Optimize Treatment Cost
Each dollar you spend in treating mine drainage is a dollar taken from your bottom line. Kroff consultants focus on driving down the overall costs of treatment for your system – whether it be chemical costs, pond cleaning, or any other outlay associated with producing regulatory-compliant discharge water.

Reduce Pond Cleaning Through Increased Sludge Compaction
Pond cleaning can be a significant cost in the treatment of mine drainage, as well as a major inconvenience. Kroff's focus on increasing sludge compaction with our treatment programs will reduce the number of times you need to clean your ponds. Increased sludge compaction will also reduce the amount of water you are paying to have removed and disposed of properly.

Improve Overall Treatment Performance
Whether mechanical performance or your chemical treatment program, Kroff will work to ensure every aspect of your system is working as effectively as possible.

Customized Outlet Compliance Programs
Kroff Chemical Company, Inc. has developed successful treatment programs to mitigate:

- Iron
- Aluminum
- Foaming
- Reduction of Solids
- Manganese
- Staining / Scaling
- Suspended Solids

You can buy chemicals from anyone. But with Kroff, you will get a partner who will provide the technical expertise and treatment solutions for your mine drainage treatment today, and in the future.

Contact Zach Rouzee, regional manager, at 304-290-9306 (zrouzee@kroff.com), or any of the mining and aggregates team members below, to discuss your application:

Mike Baker	Chris Chadwick	David Miller	Brian Yanok
C: 412-973-4847	C: 412-541-6677	C: 304-784-2638	C: 304-488-6664
mbaker@kroff.com	cchadwick@kroff.com	dmiller@kroff.com	byanok@kroff.com

MS Controls, Inc.
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Mars, PA 16046
724-625-1292
c. 412-585-5414
e-mail mscinc1@earthlink.net

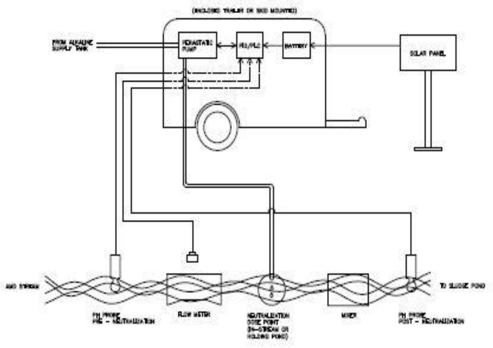
Renaissance Instruments, Inc
6609 So. Lakewood Drive
Georgetown, TX 78633

MS Controls, Inc. has been serving the instrumentation and controls market since 1997. We supply:

- High Density Lime Feed Systems
- Dry Chemical Feeders and Systems
- Strap-on Doppler Flow Meters
- Flumes and Weirs
- Metering Manholes
- Chemical Feed Pumps and Systems
- Magnetic Flow Meters
- Instrumentation Components and Systems

Solar Powered Systems and Technologies

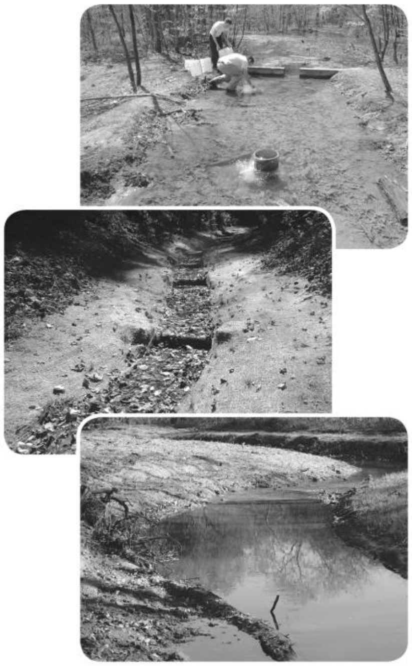
Our BlueSky chemical feed system is a recent development specifically for the AMD market. We have taken proven pH and flow measurement technology, married it to a high level on-board computer to create a self-contained pH adjustment system. The system can be skid or trailer mounted, utilizes **solar power** and can be used to run a lime silo, liquid lime feed system or to run a caustic feed pump for treatment of smaller flows.



Our REVS (renewable energy vibrator system) can be added to any existing lime silo system to improve efficiency and reduce lime waste. When properly installed, REVS cuts down on ■rat holing•, increases mixing and reduces sludge.

Other **SOLAR POWERED SYSTEM** developments include:

- Flow, pH and temperature monitoring systems with data collection
- Weather stations and rain gauges
- Variable speed drive chemical feed pumps paced by flow or pH



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