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

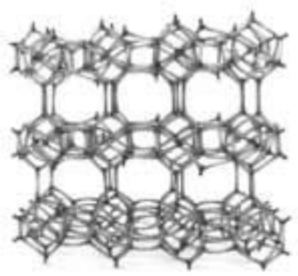
Wikipedia—What is Zeolite?

"**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.

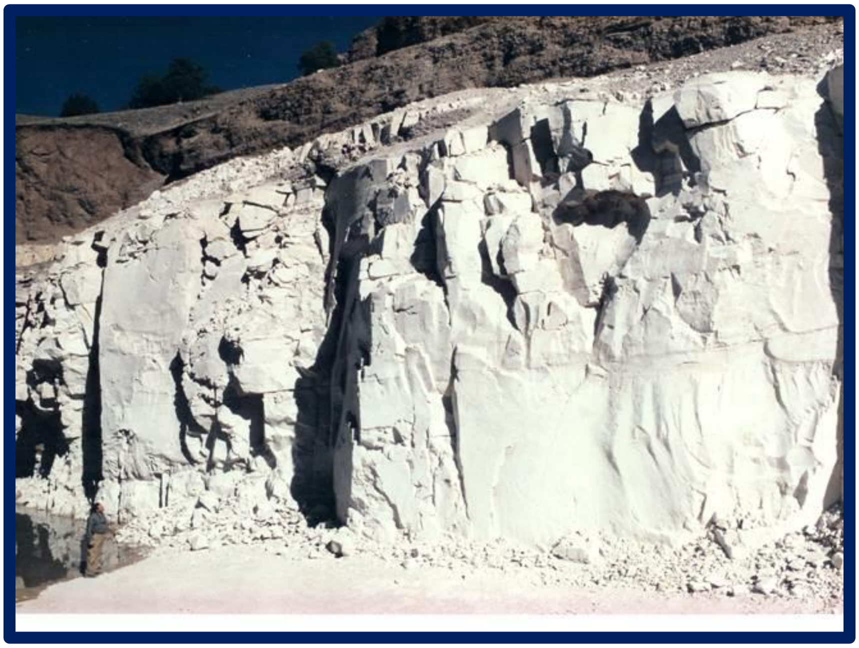
One Final Reference

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.

This was the Zeolite used for the initial tests.

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 **<u>BA</u>** part of **<u>MBBAR.</u>** 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.

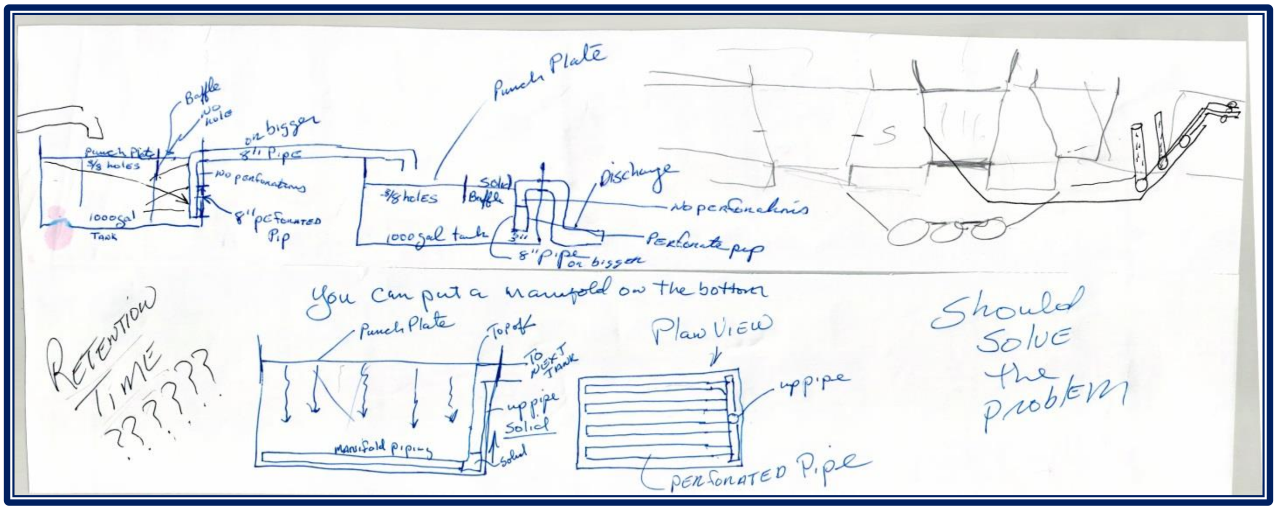
Parameter	**Raw**	**1 Min.**	**2 Min.**	**3 Min.**	**4 Min.**	**5 Min.**	**6 Min.**	**7 Min.**	**8 Min.**	**9 Min.**	**10 Min.**
Diss. Mn	**2.65**	**1.948**	**1.99**	**2.02**	**2.01**	**1.97**	**2.11**	**1.97**	**1.96**	**2.01**	**1.97**
Diss. Na	**2.99**	**15.98**	**17.06**	**17.08**	**18.17**	**18.66**	**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…..

<u>Test No.4</u>—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 <u>**Test No.3**</u>.

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>