

Low pH---Iron Oxidation

By Tiff Hilton--April 20, 2005

As you get older, you find that most of the answers to Life's many questions are generally right in front of us. The problem is that most of us can't see those answers because of the "veil of confusion" which covers our "Minds Eye". The greatest of those who went before us were able to lift those veils (also described as being laid back enough to see the forest and the trees) and were able to recognize those answers to the questions that have ultimately brought us to our current state of technological mess, I mean advance. However, it amazes me to see how such advances in "knowledge and technology" are lost and re-discovered throughout time, examples being the accomplishments of the Aztecs and Mayans. Likewise, I think the same things happens to us normal people over the course of our lives and we easily fall prey to the ever popular social disease, "HUYAS" (Head Up Your Ass Syndrome) I believe a good example of this phenomenon for us here today, which is related to Acid Mine Drainage, concerns Low pH---Iron Oxidation. WOW, Low pH---Iron Oxidation right up there next to the Aztecs and Mayans. Wellll, maybe not as significant to the advance of man kind, but Low pH---Iron Oxidation can and should play a significant role in our approach to Active and Passive treatment methodologies.

Maybe before we proceed any further, I need to answer that question racing around in your heads of "What in the heck is he talking about concerning Low pH---Iron Oxidation?". For those who know me best, it is readily apparent that I don't understand the actual chemistry of the processes connected with Acid Mine Drainage, but instead report and chronicle my observations. So, I am not here to explain or defend the chemistry associated with what I call "Low pH---Iron Oxidation", but merely report to you my observations associated with an effect which appears to be the low-pH oxidation of ferrous iron in a pH range of 2.50-3.50. My observations have shown me low pH--ferrous iron waters that lose up to 60% of their iron concentration and 40% of the acidity concentration in a matter of seconds or at most, a couple of minutes. Now, those drops in iron and acidity are exactly that, they are completely dropped from the system. In other words, within a few seconds/minutes, up to 60% (about the biggest reduction I have

observed so far) of the iron is completely removed from the water. No, the ferrous iron isn't just converted to ferric iron and still shows up as total iron in the flow, but comes up completely missing. Where does it go? That is another part of my ongoing "observations" (research) and will probably result in a follow up paper in the next year or two. Anyway, the fact that we could lose that much iron and acidity without human involvement (Active/Passive Treatment), is absolutely without a doubt, one of the most illuminating "veil lifting" experiences in my life (also called an epiphany). What upsets me is that it has always been there, and it took me 52 years before the "veil" was lifted and I saw it for what it was and am now able to utilize its "drop dead" cost benefits. I know this sounds a little bit over the top, and you may say, "Well, I knew about that--where has Hilton been?", but I don't find anyone actually quantifying this relative to treatment system integration. In fact, if one were to treat this sort of water chemically, there is little doubt based on my experiences (observations), that it would be done so near the point of discharge from the seep or deep mine seal. Based on my titration studies, if you utilize the full effect from the Low pH-Iron Oxidation process, it can result in an overall reduction in chemical consumption of 70% and a reduction in sludge volumes of 35-50%. That is simply amazing when you realize that you just saved millions (literally--calculated trust fund on 75 years), by simply providing a medium for age old natural processes to take place without human interference. In other words, the secret to success for this process is to do -----NOTHING. I know its hard not to be able to toss in some quicklime pebbles or soda ash briquettes, but you have to refrain from this practice. Some of you may even have to commit yourselves to "Betty Ford" to get over this incessant feeling of having to scientifically through technology, remediate all problems in the universe.

So, today I want to share some of my observations on a site where I have observed the "Low pH---Iron Oxidation" process in action. The site will be referred to as the "Greens Run Refuse Area Project" and is located just outside the town of Kingwood, West Virginia. It was at this site and several others, over the last couple of years, where I attained "enlightenment" concerning this type of natural remediation. Having said that, and probably more than I should have, let's proceed to an overview and

description of the Low pH--Iron Oxidation process as it occurs at the Greens Run Refuse Area.

Greens Run Refuse Area Project

The "Greens Run Refuse Area Project" is an AML reclamation project that involved sealing several old deep mine portals and regrading/revegetating refuse generated from the mining process. The majority of flow comes from wet seals (see picture below) that drops into a grouted flume (U shaped) and travels 600' (see picture on next page) over a steep slope to the valley (hollow) floor. At this point it meanders through the woods until it enters Greens Run.

Greens Run Refuse Project--Wet Seals



Greens Run Refuse Project--Flume Down Over Slope



Sorry about the snow cover, but you can see when I took this picture. I went back to Greens Run in February to see if the process was ongoing through the winter months under snow cover. It was.

The AML section of the WVDEP had analysis for this water that it collected at the top of the 600' flume and at the bottom. The raw "Top of Flume" quality over 3 sampling periods as provided by WVAML is as follows:

| Site | Date | pH | Acidity | Conductivity | Sulfates | Al | Fe | Mn |
|--------------|---------|------|---------|--------------|----------|-------|--------|------|
| Top of Flume | 2/27/04 | 2.70 | 499 | 2,250 | 967 | 28.30 | 163.00 | 1.59 |
| Top of Flume | 6/4/04 | 2.70 | 605 | 2,270 | 1,460 | 38.00 | 116.00 | 2.13 |
| Top of Flume | 9/16/04 | 2.60 | 215 | 4,600 | 1,300 | 88.10 | 404.00 | 3.76 |

The increase in metal concentrations from February to September is what one might expect to see during normal weather patterns, February being wetter than June, which is wetter than September (a normally dry month). However, there hasn't been anything normal about the last couple years and even with all the precipitation, the progressive pattern of Winter/Spring to Fall relative to metals was quite evident. I am not quite sure what that means, but maybe it's fodder for even another paper. If you look at the previous analysis, everything looks pretty normal except for one major-glaring stand-out. If you know nothing about water chemistry but possess a Rubik's Cuban type logic and common sense, you would have picked out the acidity for 9/16/04 of 215 mg/l. If this were one of those problems on an SAT or ACT test where you try to pick the number or shape that seems out of place, wouldn't the 9/16/04 acidity fit the bill? Look generally at the other parameters and note their increases. One would think that since the 9/16/04 had the highest concentration of everything, that the acidity would not be the lowest. If you thought this, you would be correct. ***This is the part of the paper when I do a brief side-bar on Acidity.***

As noted from the analysis , there seems to be a conflict with acidity and metal concentrations for 9/16/04. To resolve this problem (because it is a major problem if you are using the analysis to design a treatment system), always perform calculated acidities once you receive the lab analysis to confirm that the Lab hot acidity is close. Why wouldn't it be close? That is a subject for a paper already presented (Brent Means--3/04). Please read the paper by Brent, but for now, take my word for it that we have major problems with the EPA protocol for performing Lab Hot Acidity tests. So, lets take another look at the acidity for these three analysis by performing calculated acidities for comparison to the lab acidities.

| Site | Date | Lab Acidity | Calculated Acidity |
|--------------|---------|-------------|--------------------|
| Top of Flume | 2/27/04 | 499 | 697 |
| Top of Flume | 6/4/04 | 605 | 626 |
| Top of Flume | 9/16/04 | 215 | 1,467 |

Sort of shocking, huh, but it now makes more sense with regards to the metals. To put this in perspective, the **Average Lab Acidity is 440 mg/l** and the **Average Calculated Acidity is 930 mg/l**. Which one would you use to design a system or project treatment costs? You don't reckon that you might come up a little short by using the lab acidity, do you (440 versus 930)? I know you are about to bust, over what's causing these discrepancies, but you'll just have to wait and read Brent Means acidity paper from the Spring symposium in Morgantown last year. So, the moral to the story is never accept lab acidity values without verification through the calculated acidity methodology. With that in mind, let's get back to what's happening at Green's Run.

Next on the agenda for Greens Run is the evaluation and comparison of the analysis at the "Top of the Flume" to that at the "Bottom of the Flume".

Top Vs. Bottom of Flume--Acidity and Iron Concentrations/Reductions

| Site | Date | pH | Cal. Acidity | % Acidity Reduction | Fe | % Fe Reduction |
|-----------------|---------|------|--------------|---------------------|--------|----------------|
| Top of Flume | 2/27/04 | 2.70 | 697 | ----- | 163.00 | ----- |
| Bottom of Flume | 2/27/04 | 2.90 | 375 | 46% | 60.50 | 63% |
| Top of Flume | 6/4/04 | 2.70 | 626 | ----- | 116.00 | ----- |
| Bottom of Flume | 6/4/04 | 2.80 | 400 | 36% | 53.60 | 54% |
| Top of Flume | 9/16/04 | 2.60 | 1,467 | ----- | 404.00 | ----- |
| Bottom of Flume | 9/16/04 | 2.70 | 944 | 36% | 172.00 | 57% |

WOW! That's all I can say--WOW! No, there are no other outside influences for dilution purposes. If there were they would be quite easy to find since basically half the total flow would have to come from the outside source with an iron concentration of 0.00. Once again, using that Rubik's Cuban logic, I would have found that amount of outside infiltration into the flume and there is no such source at the site with 0.00 mg/l iron. It is safe to say that we are actually witnessing an extremely efficient natural process. This is further confirmed by the titration results and the physical appearance of the sludge itself when viewed in the following sequence:

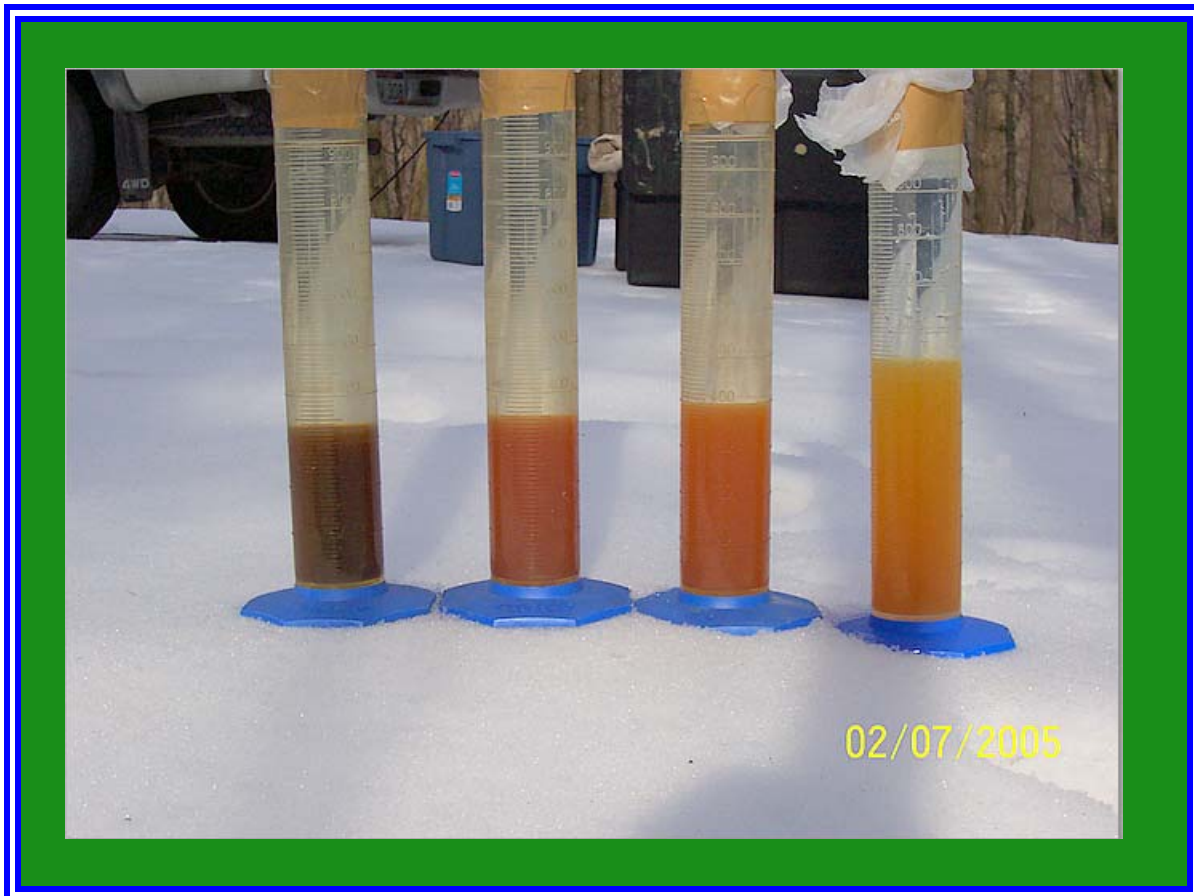
Titration No.1--Directly from Wet Seal--Dark Green Ferrous sludge

Titration No.2--At Top of Flume--Dark Orange/Trace of Ferrous Green

Titration No.3--At Mid-point of 600' flume--Orange/No trace of Ferrous

Titration No.4--At Bottom of Flume--Light Orange Ferric sludge

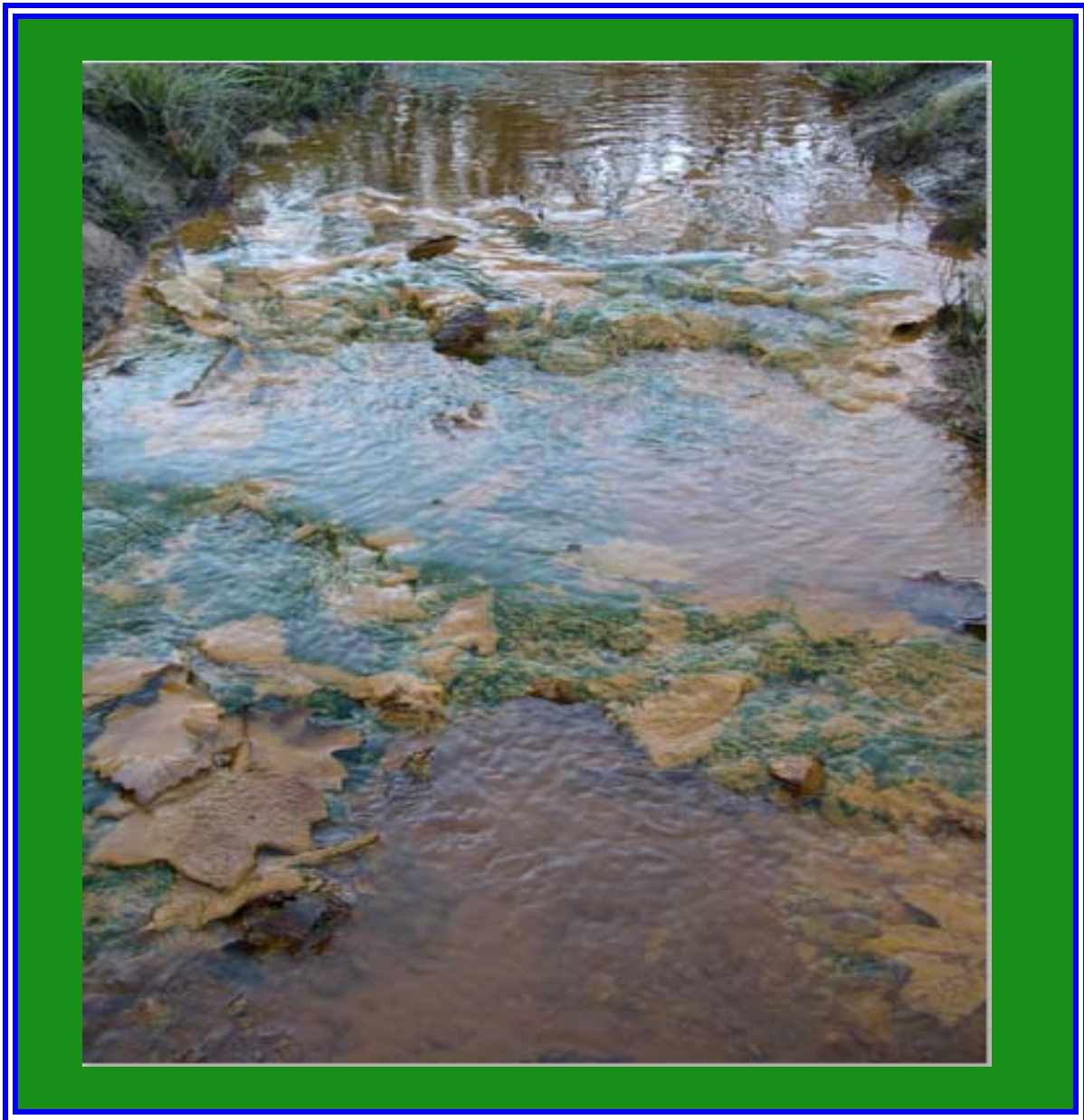
Please view the picture below as 1-4 being left to right:



The ongoing stages of oxidation from the Seals to the Bottom of the Flume is occurring within 1-2 minutes at most. To me that is significant, especially when the titration tells me that I need 70% less sodium hydroxide per gallon of treated water at the Bottom of the Flume versus the Top. So, what is happening to this water? If you are diligent enough to calculate the amount of acidity produced by the missing iron, you will note that it is quite close to the reduction in acidity. Hopefully, that would be the case, but the question still remains, "Where is it going and what's driving the process reaction?"

What force of nature could almost instantly remove iron? I have some ideas but I promised at the beginning of this paper that I wouldn't talk chemistry. Therefore, for a possible clue as to catalyst in this operation, please look at the next picture. Gregg Smith of the AML section of the WVDEP sent this to me. It is water leaving the wet seals and getting ready to turn down the hill at the Top of the Flume. Do you notice all that "Bio-Mess-Mass" stuff in the ditchline? I think part of our answer is there. Anyway, that is two papers down the road--see the following picture.

Bug Central



So, what do we do with this new-old-found information? Unless, you need further meditation time at "Betty Ford", it should be quite obvious that identification of low pH--ferrous iron AMD sources can drastically affect the Active and Passive Treatment methodology.

With respect to Active Treatment, utilization of the results of low pH---iron oxidation with respect to the location of chemical injection can reduce your chemical costs by 70%, reduce your sludge volume by 35-50%, and reduces the treatment pH from 9 (required to remove ferrous iron) to 7.

With respect to Passive Treatment, utilization of the Low pH---iron oxidation process offers an inexpensive and quite efficient method by which to rid your system of up to 60% of your total iron. Remember, iron is the primary killer of Passive Treatment systems and its elimination is the primary focus for ultimate utilization of limestone and/or sulfate reducing alkalinity producing structures.

Since actually taking note of this at Greens Run, I have seen and documented the same reductions at several other locations. I also know that Margaret Dunn and Tim Danehy of Biomost, Inc., have documented the same processes occurring at sites in Pennsylvania. As I said in the beginning, this is obviously nothing new. However, it would seem that we need to review the benefits of "Low pH---Iron Oxidation" as they relate to Active and Passive Treatment methodologies, and develop an appropriate treatment protocol to optimize these natural effects.