MN TOXICITY TO AQUATIC ORGANISMS

BY

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PREFACE

**This Paper Was NOT Written For Those To Whom It May Concern,
But To All Those Who Should Be Concerned And Aren't.**

If we are truly concerned about the preservation and enhancement of water quality for the years to come, the time is upon us, to actively pursue a legitimate course of action, that actually addresses and solves the problems we face each today. It is time that the general all purpose rules, regulations, and laws developed for all situations, be retrofitted with the necessary tools to allow for a site specific remedy, for a site specific problem. As our society has endured the greatest advancement 'in technology in the history of civilization, over the last 97 years, it has struggled to understand and control the obvious problems associated with such an advancement. As a result, we initially have developed environmental laws of a general nature to act as a catch-all in every situation. We are now learning that this type of governing does not always work in conjunction with what's good for the environment. However, because these rules have been in place for such a period of time, we are hesitant to change, even knowing that it is the thing to do. A case 'in point, relates to the manganese effluent limits associated with coal mining. As with many of the guidelines established in the early years of E.P.A., the methodology by which effluent limits were developed, was consistent with technical information and ability of that particular time. However, as time has continued, so has technology, and the means by which to further evaluate our initial findings. A tremendous amount of work has been performed in West Virginia over that last twenty to thirty years in regards to water quality associated with coal mining, and the knowledge gained from this work needs to be utilized to improve water quality. Supposedly, the limits established for manganese were derived by several different methods. One method involved the survey of several hundred coal mine discharges to determine the average manganese quality that might be expected. Another, used manganese as the surrogate to other metals. By eliminating the manganese, you would automatically insure that the others would be eliminated, **if they were present.** The only other reasons justifying the current limits *involved staining bathroom fixtures, problems in drinking water plants from Mn precipitation, and of course, manganese toxicity. Initially, no one really knew much about the actual effects of manganese, so these propositions concerning problems seemed logical to consider. However, we have come a long way since those early years, using a more scientific and rational approach in our dealings with manganese.

Perhaps the most significant discovery in recent years concerning manganese is its extremely diverse pH range in which it comes out of solution. In the titration studies I have performed with water from West Virginia, Pennsylvania, Ohio, Kentucky, Virginia, Tennessee, and Missouri, it has become evident that manganese precipitation may be classified in five different categories. The **first** pH range in which manganese precipitates is a 6.5 to an 8.8.

This is commonly called a co-precipitation with iron. In order for this to happen, the iron to manganese ratio must be quite high, in the order of 30:1 or greater. Both ferric and ferrous co-precipitations occur, although the ferric proceeds much easier than the ferrous. The **second** pH range for Mn precipitation occurs from an 8.8 to a 9. 10. Instead of an iron co-precipitation, this range is associated with a calcium co-precipitation. Nearly all the calcium comes out of solution and entraps the manganese. The third category involves a pH range of 9.1 to 10.00. Based on my observations and titration results, this accounts for perhaps 85%-95% of all mine waters. There is no co-precipitation of any kind, and it appears to be of a chemical nature only. The **fourth** category involves a pH range of 10.00 to 10.50. The **fifth** and final category consists of a 10.5 pH with a delayed reaction. For the most part, the reactions involved in categories 3 and 4 are basically instantaneous. That is, once the site specific required pH is attained, the manganese begins to come out of solution quickly. This is generally associated with a drop *in pH as hydroxyls are consumed. However, the category 5 reaction may not occur for 30 minutes, which generally leads to over-treatment by the operator. To date, I have not determined a method by which to project which category will be encountered at a particular site. In fact, a specific site, with multiple raw water sources, may have more than one category present in the treatment system.

How does all this relate to toxicity? It's related to toxicity due to the chemistry involved 'in the precipitation of the manganese. By this statement, I am referring to the toxicity associated with a high pH itself ---- By this statement, I am referring to the toxicity associated to the resolubilization of aluminum as the pH is increased to precipitate manganese --- By this statement, I am referring to the toxicity of the chemicals used to treat the water as they become concentrated at high pH levels --- And by this statement, I am referring to the increase in toxicity associated with other metals, as calcium and magnesium are eliminated in categories 2 and 5, resulting in a reduction or elimination in hardness. **These,** are the troublemakers we should be focused on, *in conjunction with determining when and what site specific circumstances might cause manganese to be toxic. The original basis on which manganese limits were established, mirrored the information available at that time. We have learned that there are many other things that are more toxic than the manganese, and unfortunately, we are usually the responsible parties for the other things. Responsible in the sense, that we create the toxic situation *in an effort to rid the water of manganese to meet current effluent limits.

Many, have done work 'in this area over the last five years, and found that manganese is not the problem we once thought it to be. With the assistance of Rob Norman from WATERS, I am *including toxicity test results recently performed on several different samples of mine drainage. The primary purpose of these tests were to illustrate the toxicity of water treated for current effluent limits, versus water that was adjusted for pH only. It is quite evident from the results, that we need to re-visit our policies concerning manganese limits, and apply site specific testing for manganese limits versus a blanket effluent limit as currently, is in place. If our goal is to improve the environment, we must stop the indiscriminate assignment of general parameters for effluent limits involving the coal industry. Over the next twelve months, Mr. Norman and I will be involved in the toxicity testing of over fifty distinct samples of mine drainage throughout West Virginia. We would hope to offer these results for review to those that are truly concerned in improving the quality of the most precious resource we have, *WATER*. In conjunction with these toxicity tests, detailed incremental titration's will be performed to illustrate the extreme diversity in pH for manganese precipitation. This information will confirm the importance of a re-evaluation concerning all ideas on water treatment in general.

As first steps towards addressing the manganese issue, a committee was formed, consisting of WVDEP personnel form the Coal NPDES section, Coal Industry representatives, Consulting companies, etc The results from this group has culminated in the development of a "MANGANESE RELIEF PROTOCOL". This protocol adopts a common sense and scientific approach towards the evaluation of manganese when considering effluent limits. A copy of this is included for your review. I want to take one further moment to thank Ken Politan, Pavanne Pettigrew, Dave VanLinde, Butch Borth, Tony Barnett, and Jeff McClure of the WVDEP for their diligent work in refining and finalizing this protocol. Obviously, an endeavor such as this would never have gotten off the ground without their support and tireless efforts.

I have tried to keep my comments brief today, in hopes that the information presented, will emphasize the clear cut need to change our approach towards the improvement of water quality. There is more data available for your review, and there will be a tremendous amount more information being generated throughout this year of 1997. 1 would implore you to continue the tradition of this great country, by being the leader in what's right for the environment rather than what's convenient. The Iron Curtain has been torn down, along with the Berlin Wall. It's now up to us that we don't find ourselves building the same type walls *in regards to environmental common sense.

Thanks for coming to the symposium this year, and thanks for **putting up with Rob and I**, especially right before lunch. That is, if I got through in time to still have lunch ---------- See you next year.

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MANGANESE RELIEF PROTOCOL

I. Eligibility. With the goal of optimizing conditions for aquatic life at certain sites, the following Protocol is suggested for determining eligibility for manganese limit modifications to an NPDES permit.

   A. Status. These modifications will be granted only to post mining sites: surface mines, refuse areas, prep plants loadouts. Post mining deep mine discharges are not eligible, as per 40 CFR 434. This status will be considered on an outlet by outlet basis.
   B. Intake water testing.

      1. A raw-water study of six (6) monthly samples must be completed prior to sampling for the treatability and toxicity tests to determine the characteristics of a representative sample. Samples

are to be taken monthly and consecutively until six (6) samples have been obtained. "NO FLOWS" are not to be counted as samples. A representative sample shall consist of a raw water in which the concentration of Mh is equal to or greater than the median as determined by the six-month study. Parameters to be analyzed *include:

a. (a) pH
b. (b) Flow
c. (c) Mn
d. (d) Fe
e. (e) Al
f. (f) Hardness
g. (g) Conductivity

2. Intake water shall then be tested for eligibility by performing Treatability Studies at pH 6.0, 7.5, and 9.0, and the following parameters will be determined at each pH level ("Total" and "Dissolved" metals will both be performed only on the RAW water. "Dissolved" metals only will be performed on the pH-adjusted water):

   a. Manganese
   b. Conductivity
   c. Hardness
   d. Acidity
   e. Alkalinity
   f. Iron (Fe)
   g. Aluminum (Al)
   h. Un-ionized Ammonia (where anhydrous ammonia is used as a reagent)

3. Intake water shall be collected and toxic screening performed on the influent at the adjusted pH levels; 6.0, 7.5, 9.0, and the upper pH variance limit in their permit if it is greater than 9.0. The chemical reagent used for pH adjustment must be the same reagent that is used on site.

4. If other factors indicate that the effluent will remain toxic despite manganese relief, further testing is superfluous. Each site shall be evaluated with the reasonable goal of habitant and aquatic life improvement. A preliminary Benthic Study shall be conducted at this time to establish a base line for invertebrate aquatic life. All Benthic Studies, including the preliminary, are to be conducted in at least two (2) sites to provide, as much as possible, a control representing the unaffected portion of the strewn prior to discharge point.

II. Permit Modification. If results of the Eligibility Tests, Toxic Screening, and Benthic

Study so indicated, the next step is to submit an application for permit modification. Each site is to be judged on a case-by-case basis. While unfavorable results from the Eligibility Tests, Toxic Screening, and Benthic Study would preclude modifying the pen-nit for manganese, favorable results do not mandate such modification. All other factors are to be considered by the Agency.

A. Permit modification issued with a forty-five (45) day Compliance Schedule to allow for sample collection and analysis.

    1. If discharge point under study has a pH variance, the variance will be revoked and pH limits modified to 6.0 - 9.0.
    2. Manganese limits modified to "Report Only" and Hardness will be added as "Report Only".
    3. Bioassay (toxicity testing) on the discharge and performed in accordance with EPA/444/4-89-001.

B. If the results of the bioassay indicate that the effluent is toxic to aquatic life, the permit shall be revised back to the pre-modification conditions. Otherwise, the pen-nit will be modified again with a two (2) year Compliance Schedule.

    1. pH limits will remain at 6.0 through 9.0.
    2. Manganese will remain as "Report Only" and Hardness will be added as "Report Only".
    3. Semi-annual benthic monitoring on the receiving stream.

        a. At a minimum, one benthic survey station will be established downstream of the discharge point.
        b. Benthic surveys shall be conducted according to EPA No. 444/4-89-002, May 1989.

NOTES: - Further toxicity testing studies may be needed on a case-by-case basis. All tests must be performed by laboratories certified in the testing procedure involved.

- All sampling locations must be mutually agreed upon by the permittee and WVDEP personnel.