Utilization of Polymerized Aluminum Coagulant Technology to Reduce Toxicity of the Wastewater from an Integrated Metal Drawing, Tempering & Electroplating Facility

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An integrated manufacturing facility, involved in the drawing, tempering, and electroplating of metal parts was required to meet strict metal and aquatic toxicity limits for wastewater discharged directly to an open waterway. Traditional methods of metal removal, suspended solids and oil and grease absorption, utilizing lime and anionic polymer, were not meeting aquatic toxicity requirements for both Fathead Minnows (*Pimephales promelas*) and Daphnia (*Daphnia pulex*). A treatment program that utilized a proprietary polymerized aluminum derivative, caustic and anionic polymer was developed for this facility. Through implementation of this aluminum-based technology, all metal, suspended solids and aquatic toxicity requirements were achieved.

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Background

A manufacturing facility located on the East Coast was required to meet strict toxicity standards for effluent discharge. Like many manufacturing locations in the Upper Eastern United States, the older infrastructure of the local communities was designed for manufacturing facilities to directly discharge wastewater (after primary treatment) into open waterways, most commonly to rivers and their tributaries. These manufacturing facilities have had to "evolve and update" their waste treatment systems to meet more stringent discharge limits.

The evolution of wastewater requirements leads to today's direct discharge limitations including indigenous organism aquatic toxicity survival requirements upon a facilities discharge. In this specific case, 100% survival of both juvenile, less than 14 day-old, Fathead Minnows (*Pimphales promelus*) and for Daphnia (*Daphnia Pulex*) was required.

Manufacturing Operations and the Impact Upon Waste Treatment

This manufacturing facility is an integrated manufacturer of metal tubing. The process operations include metal drawing, heat-treating, tempering, and electroplating.

In the metal cleaning, drawing, tempering, and heat-treating operations, oils and lubes are applied to the metal parts. The use of nitrites, borax, and sterates (fatty acid organic derivatives) are commonly used in these metal process steps. Both soluble and insoluble oils are generated from these primary metal treatment operations.

The electroplating process' produces a variety of wastewater contaminants, including; pretreatment acid-etch and alkaline cleaners (surfactants, wetting agents, and chelating compounds) and metal electroplating bath & rinse process waste (hexavalent chromium, copper, and nickel) wastewater.

In the case of heavy metals, aquatic toxicity based upon the specific ion concentration, is well known and has been regulated from the on-set of government discharge permitting. The influence of soluble organic contamination, from all of the above listed operations, is much more difficult to characterize with regards to effluent toxicity. Many organics are oxidized or reduced when co-mingled and processed through the various treatment steps. The "mixed" wastewater from the bleed-in of alkaline and acidic waste creates both "fractioned insoluble organics" which can be manually separated from treatment holding tanks, as well as "emulsified and complexed organics" that influence many wastewater characteristics including:

(1) metal hydroxide inhibition and altering cation species solubility,

(2) changing the surface tension of the wastewater, and

(3) influencing the zeta potential, or the net charge differential, of the combined waste sources.

Identified Wastewater Treatment Operations

The wastewater treatment system was engineered to handle flow rates of up to 100,000 gallons per day. Modifications have been made over the years to optimize oil separation, chrome reduction, and the segregation, batch treatment, and bleed-in of concentrated alkaline and acid cleaners.

Here is a summary of the treatment steps:

- *Metal hydroxide precipitation* via the use of lime for both pH adjustment (to a level of 9.5 to 10 standard units) providing solids conditioning/neutralization was the basis of treatment.

- *Segregated waste streams of hexavalent chromium* (reduced to a trivalent species via sodium meta-bisulfite), *alkaline cleaner batches* (pH adjusted with acid), and *spent acid batches* (pH adjusted with alkali) were all engineered to "bleed-in" to an acid/alkaline retention tank.

- *The waste sources from metal forming, drawing, tempering, and heat-treating were "oil skimmed"* and routed to the acid/alkaline retention tank.

- *Upon pH adjustment, anionic polymer induced flocculation and solids' settling was preformed in two lamella style clarifiers*.

- *A sand filter* was used for solids carryover "polishing."

- Before discharge to the open waterway (river) *a final pH adjustment holding tank was used to lower the pH to approximately 8 – 8.5 standard units* with sulfuric acid.

Wastewater treated by the above process provided "marginal" success in meeting the toxicity requirements of 100% survival for Fathead Minnows and Daphnia, for a 48-hour acute toxicity test, on 100% plant effluent.

Upon analysis of the wastewater, the following was postulated as 'likely sources' of wastewater toxicity:

- Elevated sulfates
- Soluble iron, zinc, nickel, and chrome
- Pin-floc 'break-through' of metal hydroxides past the sand filter

Untreated wastewater composites had the following parameter range variance:

Figure 1.

Parameter	**Untreated Neutralization Tank**
pH:	4 .8 - 5.6 S. U.
Conductivity	2600 - 2850 mmhos
TDS	1742 - 1900
"P" alkalinity	0 ppm
"M" alkalinity	30 - 40 ppm
Magnesium hardness	11 - 12 ppm
Calcium hardness	287 - 321 ppm
Total Hardness	298 - 333 ppm
Sulfate	1500 - 1550 ppm
Chloride	140 - 180 ppm
Iron	135 - 227 ppm
Zinc	38 - 64 ppm
Nickel	151 - 183 ppm
Total chromium	76 - 114 ppm

Based upon the weekly composites and daily grab sample analysis of the existing treatment effluent, it became obvious that the existing treatment program was not going to provide compliance with the toxicity requirements of the permit.

Proposed Treatment Program: Development and Implementation

A treatment program that could lower total dissolved solids (TDS), provide low metal concentrations, and provide a means of reducing organic contamination was the objective.

Jar-testing was performed with various coagulant aids that have some known affinity for organic absorption and enhanced metal precipitation. In addition, if the coagulant aid(s) could utilize caustic versus lime for pH adjustment, a drop in TDS would be observed.

A proprietary reacted polymerized aluminum/magnesium inorganic coagulant was selected based upon metal removal and improved water clarity. The water clarity was correlated to soluble organic [emulsified oil] removal from the treated wastewater.

A "hybrid" treatment program provided the best water quality, as follows:

1. A 200-ppm dosage of the reacted polymerized aluminum/magnesium coagulant-added to the neutralization tank.

2. Utilizing a 15% lime - 85% caustic mixture for pH adjustment to a level of 9.5 standard units.

3. Adding a 1.5-ppm anionic emulsion polymer dosage for solids flocculation at the clarifier floc-mixing tanks.

4. A final pH adjustment to 7.0 standard units, in the post sand filtration holding tank, with hydrochloric acid

The supernatant from this treatment process was very clear with a turbidity of (1-3 NTU's) and absorbed the majority of organic surfactant/wetting agents (as was evident by the lack of foaming and surface tension on the air-water interface of the treated samples.)

This treatment process would also provide for improved solids capture, as the solids composition was dense and resistant to shearing, versus the previous 'all-lime' based treatment scheme.

The treatment of wastewater composites and grab samples provided the following treated wastewater quality:

Figure 2.

Parameter	Proposed Treatment Supernatant
pH:	7.0 - 7.2 S. U.
Conductivity	2410 - 2490 mmhos
TDS	1600 - 1668
"P" alkalinity	0 ppm
"M" alkalinity	25 - 30 ppm
Magnesium hardness	10 - 11 ppm
Calcium hardness	460 - 580 ppm
Total Hardness	470 - 590 ppm
Sulfate	1150 - 1310 ppm
Chloride	160 - 200 ppm
Iron	0.01 - 0.03 ppm
Zinc	0.01 - 0.02 ppm
Nickel	0.03 - 0.06 ppm
Total chromium	0.02 - 0.03 ppm

The treated wastewater metallic(s) concentration can be considered 'relatively non-toxic.' Unlike metallics, the toxicity derived from organic components cannot be gauged by any other means other then actual aquatic toxicity tests.

Wastewater was collected on-site as two weekly composites. The proposed treatment was preformed in the laboratory, reflecting actual flow/equipment design specifications. *Accuracy in treatment was gauged to match the retention time, mixing, and dosage parameters of the treatment plant.*

Upon completion of this process, the supernatant was evaluated for acute toxicity of Fathead Minnows (*Pimphales promelus*). The following toxicity data was derived for a 96-hour acute test on both weekly composites:

Figure 3.

Mortality of Fathead Minnows
(*Pimphales promelus*)
12 fish per test/2.5 gallons per container - aerated

Exposure	control	composite 1	composite 2
1 hour	0	0	0
8 hour	0	0	0
24 hour	0	0	0
48 hour	1 (8.3%)	0	0
72 hour	0	0	0
96 hour	0	0	0
TOTAL	**1 (8.3%)**	**0**	**0**

Secondary Testing & Confirmation: On-site Testing

As the laboratory tests provided a 100% survival rate to 96 hours of acute toxicity, the program was ready for confirmation on-site using real-time wastewater conditions.

The facility collected (1) weekly composite and (1) grab sample. These samples were treated on-site with the reacted polymerized aluminum/magnesium coagulant and a 15% lime - 85% caustic mixture.

The supernatant from each test was collected and delivered to a certified laboratory for permit required testing: [a 48-hour acute toxicity for juvenile (less than 14-day old) Fathead Minnow (*Promelus Pimphales*) and for Daphnia (*Daphnia pulex*).]

As a means of comparison, actual on-site, current plant discharge wastewater was also submitted for analysis, for both a composite and grab sample event.

The results confirmed the success of the ***proposed treatment program***, as both Fathead Minnow (*Promelus Pimphales*) and Daphnia (*Daphnia pulex*) *survived at 100% (no morality) for the 48-hour permitted specification time interval.*

The ***actual plant wastewater***, with the existing lime program, *failed after 24-hours with both Fathead Minnow and Daphnia experiencing 100% mortality.*

Conclusions and Final Comments

The comparative tests of the reacted polymerized aluminum/magnesium coagulant versus the existing all-lime treatment program confirmed that applying this innovative coagulant technology significantly reduces toxicity.

Metal removal and organic absorption are two benefits of applying this proprietary aluminum/magnesium technology. In addition, a reduction is sludge volume can be gained versus the traditional lime-based treatment program.

At the time this paper was submitted for publication, the facility is in the process of re-engineering the entire wastewater treatment program. A reverse osmosis (RO) system is planned for meeting both effluent compliance and water recovery parameters.

This reacted polymerized aluminum/magnesium coagulant is specified for use as a base "pre-treatment" before the polishing RO system, to gain the benefits of organic absorption, solids conditioning, metal removal, sludge minimization, and toxicity reduction.