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A Batch of Trouble, Part 1: Wastewater Treatment Tips

Dear Advice & Counsel,
I was recently put in charge of operating a batch wastewater treatment system for a captive metal finishing company. The wastewater we treat contains hexavalent chromium, cyanide, and heavy metals, along with alkaline and acidic wastes.

There has been so much attrition at my company that there is nobody left who knows about this system, and there is no operating manual for me to consult for problem solving. As a result of some unidentified problem, I have had several batches that were not treated to compliant levels and, unfortunately, some of these were sent down the drain. Our POTW and management are very concerned. We need some guidance as to what can be done to improve our treatment system.

Signed,
N.O. Recipe

A similar letter, with a nearly identical scenario, was sent in by another finisher. His end result and plea, however, were slightly different:

... I have had several batches that were not treated to compliant levels, forcing my superiors to send the waste off-site for disposal at significant cost. Management is threatening to close our department if we don't resolve our troubles post haste.

I need help in finding out why each batch is different and so difficult to treat.

Signed,
I.M. Pressured

Dear Recipe and Pressured,
You may take some comfort in realizing that there are at least two of you with similar trouble.

Because trouble usually arrives in batches of three, I was fully expecting a third request for assistance, but because it has not arrived by my publishing deadline, we'll answer these two by going over some basic batch treatment principles and a few "tricks" as well. We will be borrowing some of the text from the AESF training program on wastewater treatment (which you should consider signing up for).

Segregation

While there are cases where compliance was achieved by simply routing "everything" into a tank and then batch-treating it, such cases are the exception, not the rule. It is highly desirable to segregate streams and treat them separately to avoid chemical unions that work counter to your desires, to improve the safety of waste treatment workers, and to make waste treatment more efficient. Typically, the rinsewaters are separated into the following streams:

a. Cyanide-bearing
b. Hexavalent-chromium-bearing
c. Chelated

d. Acidic/alkaline
e. Concentrated wastes
f. "Clean" rinsewaters

Concentrated wastes include spent cleaners, acids, chromates, stripping solutions, and plating solutions that have been hopelessly contaminated.

Clean rinses are rinses that routinely contain regulated pollutants at concentrations below regulated amounts and may only require pH adjustment. They usually are few in number, but they should be identified and routed to final pH adjust system and sent down the drain. An example might be the rinse after a soak cleaner for aluminum. Such a rinse may only require pH adjustment and will contain aluminum, a non-regulated light metal.

Tank Agitation

Mixing of reagents for wastewater treatment is crucial to success. Excellent agitation of reaction tanks yields control meters that function better, and reactions that go closer to completion (closer to the theoretical "residence time" of the reaction tank). Mechanical methods for agitating a reaction tank include propeller ("prop") mixing, eductors, recirculating pumps, and air agitation. Of these, "prop" mixing is by far the method of choice, because the others typically are inefficient for mixing large tank volumes and/or release gases and mists.

Imagine a tank of water that is dyed green, and tap water is brought into the top of the tank in one corner and allowed to flow out the top at the other corner (with no mixer present). Theoretically, it would take an infinite amount of time for the entire tank's contents to be free of dye.

If we repeated the experiment with a propeller mixer running, you would always have a homogenous mix of green and clear water. The corners, top, and bottom would be the same color. It would still take an infinite amount of time to get rid of all the green dye, but all of the dye and water would be at the same concentration all the time, in all parts of the tank.

This is what we want in our reaction tanks—the same thing happening all the time. By mixing, we cause the reactants to enter into a chemical reaction at essentially the same rate in all places inside the reaction tank. We then can use theoretical residence times with appropriate safety factors to yield a reaction time that will be as near to completion as is practical with the floor space and money available.

You can purchase dyes that will allow you to verify the performance of your mixer. Pour in the dye and see how long it takes for the tank to become a uniform color. If it takes more than 10-15 minutes, your tank mixer needs a performance boost (larger prop, larger motor or an additional mixer).

Precipitation of Heavy Metals

Many but not all metals will precipitate on neutralization and not all metals will precipitate at the same pH point and to the same extent. In view of the low discharge limits with regard to soluble metal content of a metal finishing effluent, the initial problem in separation may be to decide what pH to aim for to reach the most complete precipitation of the metals present in the waste. Some of the metals that may be present are amphoteric and, therefore, are soluble at alkaline pH. An example of such a metal is zinc. Some other metals may require a relatively high pH to reach minimum solubility. This would include nickel, copper and sometimes cadmium.

By adjusting the pH to a pre-determined value (established by laboratory experiments), dissolved metals are converted to metal hydroxides that tend to be highly insoluble, dropping out as finely divided particles. However, some metal hydroxides have a high enough solubility, and some wastes contain compounds that resist conversion of dissolved metals to metal hydroxide. Some of these compounds are EDTA, NTA, citrates, tartrates, gluconates, ammonia, ammonium compounds, and more. In such cases, even after pH adjustment, enough metal may stay in solution so that regulatory limits cannot be achieved, even after the best clarification or filtration. In such cases, the wastewater is first adjusted to the optimum pH for metal hydroxide production and then a special additive is mixed in to convert the remaining dissolved metal to a sulfide instead of a hydroxide. We will discuss such additives shortly.

What to Use to Adjust pH

Several materials can be used to neutralize acidic wastewater containing the reduced chromium, including sodium hydroxide, calcium hydroxide, sodium carbonate, magnesium hydroxide, and combinations of these alkalis. Sodium hydroxide, sodium carbonate, and magnesium hydroxide do not add to the sludge volume by forming additional metal hydroxides, while calcium hydroxide (lime) precipitates as calcium sulfate and un-reacted hydroxide, thereby adding to the sludge volume generated.

There is evidence, however, that sludges formed by neutralization with calcium and/or magnesium hydroxides have lower leachability than others, may settle better in a clarifier or settling tank, and may perform better in the presence of chelates. Calcium and magnesium hydroxides also have a disadvantage in that they are not water soluble. A "slurry" must be added, creating pump and tubing clogging problems. Magnesium hydroxide has limited alkalinity, so you cannot adjust to a pH greater than about 5.5 with this material. Both calcium and magnesium hydroxide react slower with acids than sodium hydroxide, so additional mixing time is required with these materials.

Typical acids used for pH adjustment are sulfuric and hydrochloric. Acids react very quickly. Ten minutes of retention time is adequate.

Comparative Solubilities

Shown in the accompanying table is the comparative solubility of certain metal hydroxides and sulfides obtained from USEPA. The lower Ksp value (10^{-23} is lower than 10^{-8}) indicates a lower solubility. For example, lead, precipitated as the sulfide, is almost five times less soluble than lead precipitated as the hydroxide. Lead-bearing waste may therefore be treated to lower levels of concentration when pH adjustment and addition of a secondary (sulfide-containing) compound is conducted. Some heavy metals (notable trivalent chromium) are more soluble as the sulfide than the hydroxide, so laboratory testing should be conducted to ensure that treatment with these compounds will render **all** regulated metals below the regulated limits.

One of the most commonly used secondary precipitation compounds is an organic sulfide that falls into the carbamate family.

Comparative Solubilities

Compound	Solubility Product
Zinc Sulfide	1.2×10^{-23}
Zinc Hydroxide	1.7×10^{-6}
Chromium Hydroxide	1.2×10^{-8}
Lead Sulfide	3.4×10^{-28}
Lead Hydroxide	6.7×10^{-6}
Cadmium Sulfide	3.6×10^{-29}
Copper Sulfide	8.5×10^{-45}
Nickel Hydroxide	6.9×10^{-3}
Nickel Sulfide	1.4×10^{-24}

These are sold commercially with numerous trade names, but in general they all function by converting metals that remain in solution to sulfide compounds. A generic name for these precipitating compounds that is commonly used in the metal finishing industry is "DTC" (from di-thio-carbamate). DTC has a fairly low toxicity and is reported to degrade rapidly upon discharge into the environment. However, at least one case of a large discharge to a POTW has caused an upset and severe fish kill. The storage and use of DTC must be carefully controlled.

Stoichiometric amounts of DTC may lower heavy metal concentrations to 1 mg/L, while a 10% excess may achieve concentrations below 0.1 mg/L. Cationic polymers are recommended for use with DTC, making for an effective one-two punch for removing heavy metals.

A major problem that "Pressured" had was the presence of lead in the raw wastewater. Simple pH adjustment did not bring the lead concentration into compliance, but use of DTC was successful.

Both "Pressured" and "Recipe" had a number of additional problems that we will cover next month. *P&SF*

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