Chemical Precipitation Wastewater Treatment Systems

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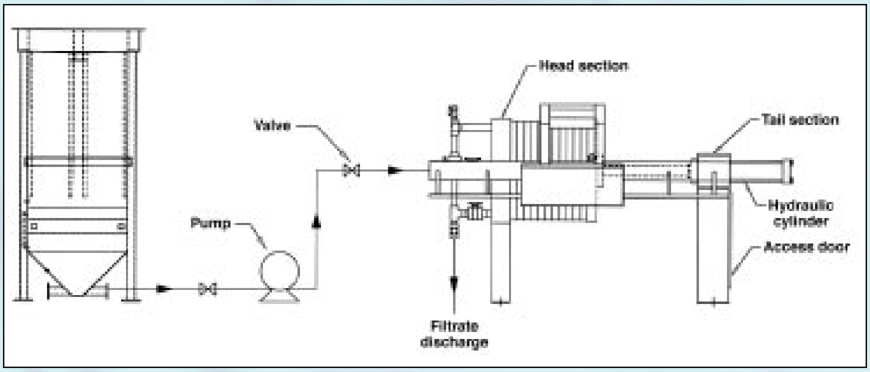
As federal and state regulations cause sewer discharge limits to become more stringent, the chemical precipitation wastewater treatment systems currently in use will become inadequate, and their performance will need to be improved. What follows is a look at these systems and how performance can be improved.

For all practical purposes, a hydroxide precipitation wastewater system is a chemical manufacturing facility. Its purpose is to convert process waste chemicals and byproducts from manufacturing into:

1. A non-hazardous form (such as converting cyanide to carbon dioxide and nitrogen gases).
2. An easier-to-handle form (such as converting soluble metal salts to insoluble hydroxides that can be filtered out of the solution and disposed of safely).

The efficiency of this process must be better than 95 percent and yield an acceptable product—effluent acceptable for discharge and waste that is suitable for disposal:

- 100 ppm must be reduced to 1 ppm—99 percent yield.
- 40 ppm must be reduced to 1 ppm—97.5 percent yield.



Clarifier/filter press system.

Everyone involved in production knows that this goal is not easily achieved.

At the heart of performance in a waste treatment system are three factors: Chemistry, equipment and the operator.

Chemistry

Consider the following reaction: Nickel sulfate ($NiSO_4$) + sodium hydroxide (2 NaOH) = nickel hydroxide (Ni $[OH]_2$) + sodium sulfate (Na_2SO_4). Add sodium hydroxide to force the reaction to the right. To force it to the left, add sulfuric acid to decrease sodium hydroxide.

At high pH, the reaction vessel contains nickel hydroxide, sodium sulfate and sodium hydroxide. At low pH, it contains nickel sulfate, sodium sulfate and sulfuric acid. This demonstrates several chemical principles:

1. Most chemical reactions are reversible (the destruction of CN by chlorination reaction is pH sensitive). A chemical reaction's yield is rarely 100 percent.
2. Chemical reactions seldom extend to completion.
3. Chemical reactions are influenced by one or more of many factors (*e.g.*, temperature, concentration, pH, reaction time).
4. Chemical reactions need a driving force to proceed in a particular direction, such as:
   (a) Formation of water;
   (b) Release of gas;
   (c) Formation of insoluble products;
   (d) The presence of one or more components in excess of the stoichiometric ratio.

Of the factors that control chemical reactions, the easiest to demonstrate is pH. Destruction of cyanide is a two-step reaction. With the addition of chlorine (sodium hypochlorite) at pH 11, cyanide is converted to cyanate. At pH 8.5, cyanate is converted to carbon dioxide and nitrogen, with the addition of more chlorine:

$2\ NaCN + 8\ NaOH + 5\ Cl_2 = 10\ NaCl + 4\ H_2O + 2\ CO_2 + N_2$

Destruction of Cyanide by Chlorination

$NaCN + Cl_2 = NaCl + CNCl$ (cyanogen chloride)
$CNCl + 2\ NaOH = NaCnO + NaCl + H_2O$
The total of these two reactions can be represented as follows:
$NaCN + 2\ NaOH + Cl_2 = NaCNO + 2\ NaCl + H_2O$

$2\ NaCNO + 4\ NaOH + 3\ Cl_2 = 2\ CO_2 + 6\ NaCl + N_2 - 2\ H_2O$
In the same manner, the total of these two reactions can be represented as:
$2\ NaCN = 8\ NaOH + 5\ Cl_2 = 10\ NaCl + 4\ H_2O + 2\ CO_2 + N_2$

For complete reaction, one pound of cyanide $(CN)^-$ requires 7.3 lb of sodium hydroxide and 8 lb of sodium hypochlorite to produce 12 lb of soluble chemicals.

While cyanide is converted to cyanate, carbon dioxide and nitrogen at pH 8.5, the reaction is slow and reversible. At pH 8.5, residual cyanide can remain in existence in the reaction tank in spite of the presence of excess chlorine. Cyanide forms some strong and very stable complexes, such as ferrocyanide, that are nearly impossible to destroy.

In the article "Chasing Those Elusive Cyanide Ions," (Nov. 1992 issue of *P&SF*) it is stated that: "Laboratory tests on the effluent from our two-stage alkaline chlorination process gave us some most interesting data; cyanide was not being completely destroyed in the reactor." The same article further states that initial 2.7 ppm cyanide in an unpreserved sample aged for nine hours showed 1.4 ppm cyanide.

To optimize the chemistry of the process, therefore, reaction conditions must be fine-tuned. The best way to accomplish this is in the field, so that all variables and characteristics of a particular system can be taken into account.

Equipment

Equipment design and placement influence the chemistry of the process, and the efficiency of the system. Undersized tanks adversely affect reaction time, and poor agitation can result in non-uniform pH, temperature and chemical concentration throughout the vessel. These are the factors most critical to system efficiency. If the system is designed to handle 2,000 gal/day, it may perform satisfactorily up to 3,000 gal/day. It will not perform satisfactorily, however, if the load goes too high (for example, 10,000 gal/day).

A filter press will perform best when solids exceed two percent. It should be installed to feed from the sludge side of the clarifier. It is inefficient to use a filter press as a polishing filter.

Probes should be calibrated according to the manufacturer's recommendation at least once a week. Filters should have a prescreening device. All meters, monitors and controls should be kept in a clean and dry place. Most of these monitors carry signals in the mV range that can easily stray or short out unnoticed, especially over distance or in the very humid atmosphere characteristic of plating shops.

1 lb Disodium Copper Cyanide $Na_2Cu(CN)_3$:

.417 lb CN	x	7.3	= 3.00 lb NaOH
	x	8.0	= 3.33 lb NaOCl
	x	12.0	= 5.00 lb NaCl, soluble
.246 lb Na	x	2.52	= .62 lb NaCl, soluble
.337 lb Cu	x	1.54	= .52 lb Cu(OH), insoluble

Before considering an upgrade of the treatment equipment, take another look at the production process. Usually, the problem becomes just as big when a problem contaminant reaches the main discharge stream. One gal/min of 100 ppm oily discharge mixed with a nine gal/min oil-free stream will produce a 10 gal/min stream that contains 10 ppm of oil. It is advisable, therefore, to isolate problem streams while they are still easy to contain. In many cases, the recovered chemicals may be suitable for reuse or recycle. Care must be taken, however, before recovered chemicals are recycled. After they are purified, tests should be performed to ensure that these chemicals are suitable for recycling.

By using spray rinse, the following benefits may be realized:

- Improved quality resulting from improved rinsing.
- A reduction of the chemical loading on the treatment system.
- Closed-loop rinse cycle becomes a viable option.

Operator

As mentioned previously, the operator must have a good knowledge of the chemical principles behind the treatment process, as well as a good understanding of the equipment, its function and how to maintain it. This could not be manifested better than in the case of the nickel/chromium strip solution, where any chromium salts left over in the filter will redissolve in the high pH solution used for nickel precipitation, producing chromium-contaminated effluent. Pumps will not operate with clogged strainers, and we all know what happens if they are run dry. Likewise, pH probes will not work if stored dry or in the wrong solution. The fact that a pH probe works does not mean it is accurate.

Good housekeeping, operating practices and a daily activity log are indispensable for the successful performance of the system. Changes may happen very slowly and can be almost impossible to detect without looking back at the record. Frequently, operational difficulties can be detected by charting analysis results or chemical use. Certain routine activities, such as replacement of filter cartridges, probe cleaning and calibration, should be just that—**routine**.

Its Time Has Come

Hydroxide precipitation systems used to be the “Best Available Technology.” It is time, however, to take advantage of new, environmentally friendly technology. Hydroxide precipitation systems are best used for batch treatment of concentrated waste streams produced by other technologies, such as concentrates separated by nanofiltration membranes or ion exchange resin regeneration liquor.

There are too many variables that control the operation of hydroxide precipitation systems. This is the reason for their poor performance. In defense of the operator, all of the variables are not in his control. Hydroxide precipitation, the oldest and most cumbersome wastewater treatment technique, produces the most waste. One pound of sodium copper cyanide consumes 6.33 lb of chemicals to produce 2.5 lb of filter press cake that contains 20 percent solids. In addition, the five pounds of soluble chemicals produced, added to total dissolved solids (TDS), henders recycling efforts. As new technologies develop and existing technologies become more affordable, consideration should be given to on-line treatment where chemicals are recovered from rinsewater and returned to the process tank.

Environmental professionals should adopt water recycling, chemical recovery and zero water discharge principles. It's a good alternative to using chemicals to stabilize other chemicals to produce sludge and high TDS wastewater that is not fit to be discharged into the environment. P&SF

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