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A Batch of Trouble, Part 2: Wastewater Treatment Tips

Continuing our response to "Pressured" and "Recipe" from the May issue, let's take a peek at Pressured's treatment system.

The waste treatment system included three large batch treatment tanks, approximately 4,000 gal in size (see Figure). Two tanks were used for pH adjustment/metal precipitation and one tank was used for cyanide oxidation. Each tank was equipped with a mixer that appeared to be of suitable size to adequately mix the contents, and a pH meter. The cyanide oxidation tank also was equipped with an ORP meter.

Each tank was equipped with a drain valve at a location of about 40 percent of the tank height. These valves did not appear to have been used in some time, and were likely inoperable.

Each of the three treatment tanks was equipped with drain valves that route treated waste to one of two plate-and-frame filter presses, approximately 15 cubic feet in capacity. The water discharged from these filter presses had two routes, depending on operator decision:

(a) Discharge was routed to the floor where drains collected the flow and pumped it back to one of the two pH adjust tanks;
(b) Discharge was routed to sewer.

The solids collected by the filter presses were sent off-site for disposal.

Filter press number 1 had a discharge manifold that, at one time, included a valve and piping for routing filtered water back to any one of the three treatment tanks via a header and valves, but this had been disconnected and capped.

In addition to the three large treatment tanks, there was a much smaller tank equipped with a mixer for treatment of wastewater that contained hexavalent chromium.

While there were tanks suitable for mixing up treatment chemicals and feeding these reagents into the treatment tanks, the feed pumps were broken and reagents were added manually.

A lime mixing tank was present, but not in an operable condition. It had been disconnected from the treatment tanks because of clogged of valves and piping.

The facility had an on-site laboratory equipped with a pH meter, filtration equipment, and atomic absorption spectrophotometer to test treated batches and confirm compliance.

Treatment & Chemicals

The following treatment methods and chemicals were used at this facility:

Chromium Reduction

Chromium was reduced using sodium bisulfite and sulfuric acid (if necessary).

Cyanide Oxidation

Cyanide oxidation was conducted in a single stage using sodium hypochlorite and lime (if necessary).

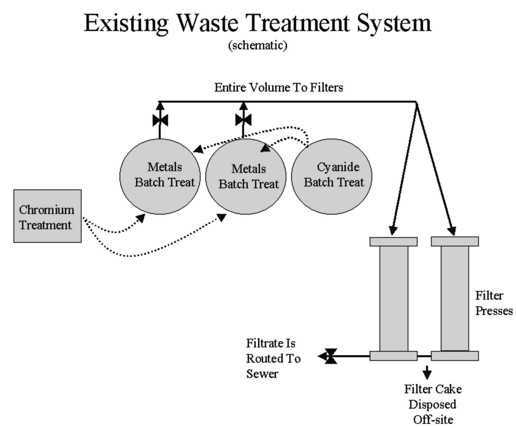
Metal Precipitation

Metal precipitation was conducted by adjusting the pH to 9.0–9.5 with lime (calcium hydroxide). If dissolved metals are not rendered sufficiently insoluble by pH adjustment alone, a combination of DTC and formaldehyde, along with a polymer, were added.

Wastewater Treatment Method

The wastewater treatment method was one that had been handed down verbally through numerous operators over time. There was no manual to provide guidance for conducting this treatment or maintaining the equipment.

The following were the waste treatment methods employed:



Chromium Reduction

The pH of the waste was checked and reduced to less than three with sulfuric acid. Sodium bisulfite was then added until the operator visually confirmed a completed reaction by the color of the treated wastewater. The treated batch was then pumped to either of the two pH adjust tanks.

Cyanide Oxidation

The pH was checked and adjusted to 12. if necessary. Sodium hypochlorite was then added until an ORP meter indicated a reading of 300 mV. The batch was allowed to react for an hour before it was routed to one of the two pH adjust tanks.

Metal Precipitation

The pH was adjusted to 9.0–9.5 using lime. The lime powder was added manually over the side of the tank. If too much lime was added, sulfuric acid was added to lower the pH. A sample of the wastewater was taken to the on-site laboratory to confirm that the dissolved metals met federal/local limits. If the laboratory testing indicated that the heavy metals did not meet limits, a secondary treatment was conducted. This secondary treatment included the addition of three reagents: DTC, a polymer, and formaldehyde. The dosage was based upon past experience. After mixing these additional chemicals into the batch, a second sample was tested in the lab for compliance. The addition of DTC/polymer/formaldehyde was repeated if necessary.

Filtration

The entire volume of a successfully treated batch was filtered through two filter presses. Until recently, all of the filtrate from the filters was discharged to sewer. On the (good) advice of another consultant, a change had been made so that the initial filtrate from the filter presses was no longer discharged to the sewer, but was routed back to the pH adjust tanks until the filtrate was clear enough to discharge to sewer.

Recommendations

The following were recommendations for improving the equipment and treatment methodology at this facility:

Chromium Reduction

While a visual check to verify that all hexavalent chromium is reduced to trivalent can be a suitable way to go, we recommend that verification by testing be conducted. A beaker of treated waste should be adjusted to pH 8–9 with sodium hydroxide solution and allowed to sit undisturbed for 15 minutes (a drop of polymer can be added to facilitate settling of the solids). The clear liquid at the top can then be inspected for the presence of any yellow coloration. As little as two ppm hexavalent chromium will yield a yellow color that can be visually detected, or the clarified liquid can be analyzed for total chromium with the atomic absorption spectrophotometer.

The operator must confirm that the waste is below pH 3.0 before adding the sodium bisulfite to ensure a complete reaction. This can easily be done with the pH meter that is available in the laboratory.

Cyanide Oxidation

(a) Assuming that a reading of 300 mV on the ORP meter confirms destruction of the cyanide may not yield consistent results. While ORP meters are excellent methods of verifying (and controlling) treatment, we recommended that the operator also use potassium iodide-starch test papers (available from scientific supply houses) to confirm that the ORP reading is positively verifying cyanide destruction. These test papers turn blue in the presence of an oxidizer, such as chlorine. The darker the blue color, the more excess chlorine is present. To use these papers, dip one strip into the wastewater for five seconds and observe the color obtained:

- Faint Blue: Slight excess of chlorine (2-5 ppm)
- Sky Blue: Normal amount of excess chlorine (5-10 ppm)
- Dark Blue: Above normal amount excess chlorine (20-50 ppm)
- White with blue stripe: High excess (100+ ppm)

Note: If the paper stays completely white, the most likely case is that you do not have enough chlorine to adequately destroy the cyanide, and you must adjust your system accordingly. Because a very strong excess of chlorine (10,000 ppm) can also turn the paper white (through bleaching action), you should first dilute the wastewater 10:1 then re-test. If the re-test stays white, you most likely need to increase the chlorine addition rate. If the diluted wastewater tests blue, you are adding way too much chlorine and need to make a major cut-back.

While the reaction between cyanide and chlorine proceeds, the test papers should show a blue coloration through the entire hour of reaction time. If a negative (white) test is obtained, more hypochlorite should be added until the papers turn blue again.

(b) The chemical feed system for adding hypochlorite and sodium hydroxide or lime to the reaction tank should be repaired as soon as possible to allow the operator to conduct his/her work more efficiently and safely.

Metal Precipitation

(a) Use of formaldehyde to treat the types of waste collected at this facility appeared to be unnecessary. Formaldehyde is a reducing agent that may be helpful in breaking up some metal complexes in some wastewater streams, but the DTC (in combination with the polymer) should do this equally as well in the absence of formaldehyde. We recommended treating a troublesome batch using the same technique as currently used, but to leave the formaldehyde out. Successful treatment can be verified in the laboratory. Formaldehyde has significant health hazards and, therefore, should not be used unless absolutely necessary. Subsequent batches were successfully treated without formaldehyde.

(b) Because the waste treatment system was designed to use side taps to discharge a large portion of the treated wastewater, the side taps should be repaired to usable condition, and a system for collecting such drainage and sending it to sewer should be installed (sump, pump and piping with valves routing the water to sewer or back to the treatment tank). These side taps can be employed to drain the clarified water from each tank and send it directly to the sewer (assuming it is in compliance). This will reduce volume loading on the filters and allow for more batches to be treated each day, or more time to treat a given batch.

After treating a batch, it should be allowed to settle. A jar test can be conducted to verify the level at which the solids will settle, confirming the ability or inability to use the side taps. If the solids should drop below the side taps, a sample can be drained to the sump and tested for compliance. If compliance is achieved, the tap can be opened and the drainage can be routed to the sewer. If compliance is not achieved, the water collected in the sump should be returned to the treatment tank.

(c) The volume of flow to the wastewater treatment system is currently too high, allowing only slightly more than two hours for treating a batch. We recommended that a water usage survey be conducted to identify and correct sources of excessive volume flow.

(d) Chemical mixing tanks and delivery systems need to be repaired so that chemicals are not added manually.

Filtration

(a) The capped-off return pipe and valve system should be restored to good working order. This will allow the operator to return the filtrate back to the source.

(b) The initial flow from the filters can not be routed to the sewer, because this discharge is extremely high in metals content and will cause a significant violation of discharge limits. Only when the filter discharge is clear enough, and lab tests have verified compliance, can the discharge be sent to the sewer.

(c) The filter cloths should be inspected and replaced, if there is any damage evident. In any case they should be replaced annually.

(d) A solids thickening tank should be installed to allow drainage of solids from the pH adjust tanks to the thickening tank. The filter presses would then operate from this thickening tank instead of the pH adjust tanks. This will greatly improve the efficiency of the presses and reduce filter press cycle times (usually by 50 percent). The client has several large tanks on site that may be suitable.

General Recommendation

A detailed manual describing the operation and maintenance of each component of the waste treatment system should be produced.

Next month we will go over Recipe's problems. *P&SF*