REMOVAL OF HEAVY METAL IONS FROM OILY WASTEWATER

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Oily wastewaters are generated by manufacturing processes where machine coolants, hydraulic fluids, and aqueous degreasing solutions come into contact with rinsewater. The ideal wastewater treatment segregates oily wastewater from metal ion bearing wastewater, but in operations of the type just mentioned this is sometimes impractical and the metallic wastewater may already be oily anyway. This presentation is a case study of lessons learned during one attempt to successfully treat oily wastewater which contained both metal ions and oil in quantities over the discharge limits.

Oil and Grease

Oily waste in water is measured in terms of its extractability by hexane or Freon (TM), but other solvents such as ethyl ether, carbon tetrachloride, and petroleum ether have also been used as extractants. Greases are generic, semiliquid materials which include fatty acids, soaps, waxes, fats, and other similar extractable materials.

Oily wastes typical in a manufacturing plant include aqueous machine coolant with either synthetic or water soluble oil, grinding oil, cutting oil, lubricating oil, hydraulic fluid, lubricating grease, and oily soil from the plant floor. In the case study plant, these oils and greases contaminate water through machine cooling and through cleaning up minor spills and machine leaks on the shop floor.

Oils and greases are defined in three ways: polarity, biodegradability, and physical characteristics. Polar oils and greases are derived from animal and vegetable materials and are usually found in the food-processing industry. However, a cooling oil used in the case study plant was found to be of this type. Oils and greases derived from petroleum or minerals are nonpolar. Generally, polar oils and greases are biodegradable while nonpolar materials are bioresistant.

Physical characteristics of oils and greases are described in five categories:

1. Free oil - rises rapidly to the surface under quiescent conditions.
2. Mechanical dispersions - are fine droplets ranging from micron size to several millimeters and are stabilized by electrical charges or by pump action.
3. Chemically stabilized emulsions - are droplets of oil which are stabilized by surface active agents at the oil/water interface.
4. Dissolved oil - is truly soluble in the chemical sense plus very finely divided oil droplets measuring 5 microns or less in size which defies removal by physical means.
5. Oil-wet solids - is oil that has adhered to the surface of particulate matter in the wastewater.

In the case study, plant oil and grease in untreated wastewater varies up to 30,000 mg/l. When the wastewater treatment plant was initially installed it was discovered that oils and greases varied up to 750,000 mg/l (we were attempting to treat watery oil) and these levels clearly interfered with heavy metal removal.

Sources of Metal Ions

Finding all the sources of metal ions in wastewater proved to be challenging. After much analysis of each wastewater stream, we gradually developed an understanding of the sources. The obvious sources were pickling baths, chromate conversion coating rinses, and alkaline cleaning baths associated with metal surface preparation. Less obvious were sonic cleaning baths, mop water, floor scrubber water, and machine coolant. The point is, be sure you thoroughly characterize your wastewater before committing to a design.

Separation of Waste

Prior to the wastewater treatment system installation, the case study plant had a single collection point for any liquid waste not characterized as hazardous by EPA hazardous waste regulations. Whether watery oil or oily water, all wastes were emptied to one sump which was pumped into the holding tank of an ultrafiltration unit. The permeate was shipped off-site as a non-hazardous oily wastewater while the concentrate was shipped as waste oil.

Once the decision was made to treat wastewater on-site for release to the public sewer, the oily waste was combined with the rinse water from the metal cleaning line which was oily also. The first step toward consistent treatment was to separate many of the waste streams into waters and oils. Those streams designated as oils are now collected in a sump for the waste oil tank while the oily waters are collected in a sump that feeds an oil-water gravity separator. Water from the separator and water from the metal finishing room are held jointly in either of two 8,000 gallon equalization tanks until treated. A significant portion of oil, that which adheres to the surface of settleable solids, is removed in the gravity separator. Typically, the oil and grease load of water in the clean well is 2,500 mg/l or less.

Although the performance of gravity separators are theoretically predicted by Stokes law, turbulence and shortcircuiting make proper hydraulic design and retention time the critical design factors. As you may guess, longer retention times allow better separation. In the case study, we selected a corrugated plate interceptor due to limited floor space.

Neutralization

Neutralization of oily wastewater turns out to be the critical operation when heavy metal ions are being removed. At the optimum pH, the metal ions precipitate with ease; at too high or low pH, the system becomes hard to control. Neutralization curves developed in laboratories and reported in technical literature proved to be inaccurate in practice. Therefore, we developed neutralization data unique to the problematic wastewater we are dealing with. This is the trick to successful design of a wastewater system.

The trick of effective operation is to select electrodes that require the minimum of cleaning. Even so, with oily wastewater, daily cleaning of pH electrodes is recommended. The oil quickly stops up the membrane through which water passes and an incorrect pH may be indicated.

After 18 months of fighting leaky fittings and sulfuric acid spills, we installed a carbon dioxide system for lowering pH. The neatest thing about this is that 5.5 is the lowest pH achievable, so we have eliminated the volcanic overshooting possible with poor sulfuric acid control.

Coagulation

Excess sodium hydroxide (NaOH) precipitates the metal ions as hydroxides in the standard way. The chief problem in the coagulation of the metal precipitates in oily wastewater is that the oil greatly adds to the volume of the floc and consumes chemical. Therefore, when setting chemical dose, one has to account for the chemicals needed to coagulate the oil as well as for the metal hydroxides. Most of the time, the chemical dose required for oil removal is 10-20 times the dose needed for metal hydroxide coagulation.

Dissolved Air Flotation

Because we were dealing with large volumes of oil compared to metal hydroxides, we decided to float the sludge instead of clarifying water by gravity settling. Dissolved air flotation (DAF) works well as long as the air flow and recycled water are balanced carefully with incoming chemically treated water. We had to modify the recycle design slightly to make it work optimally. Since making the modification we have had very few DAF control problems.

Media Filtration

Some solids always come off the DAF overflow so a media filter is needed to capture these solids. Before we learned to control the DAF we had to change media every third month. Now, with better DAF control, we have operated on the same media for nearly ten months with only a minor loss of flow rate observed. Media selection does not seem to be critical, but we use garnet and anthracite.

Carbon Filtration

We also installed a set of carbon filters to capture any toxic organics which may pass through the wastewater plant. It takes only four ounces of a chlorinated cleaning solvent to violate the discharge limitation for toxic organics. The carbon filters serve as a safety net for minor spills or minor contamination of wastewater, but they are not meant to be a primary treatment unit for organics; therefore, strict administrative procedures have been implemented in the shop to prevent contamination of wastewater.

Operational Problems

During the first 18 months of operation, the chief problems were overcoming vast operational and maintenance problems encountered by an inexperienced crew. There were so many problems at first that we were unable to identify root causes for all the symptoms. Therefore, we began by attacking symptomatic problems and looking for what else happened when we changed something. Gradually the operators began to understand the complexities of the system and to get a handle on how to operate it effectively.

Chemical Selection: One of the first problems attacked was to select optimum chemical treatment. However, as we proceeded, major process changes made to the treatment plant caused the chemical needs to change. For instance, in the early days of startup we used an emulsion breaking chemical in large quantities, but as we did a better job of segregating watery oil from oily water the need for this chemical disappeared. Another example has been the evolution of the coagulant. We started with ferric chloride and evolved through four other products to an organic polymer based coagulant.

Jar Testing: In order to stay on top of chemical dose, we run a jar test for each treatment batch. At the very least, the amount of coagulant varies from batch to batch, but the wastewater is so variable that we have to stay alert to changing needs for coagulant type also. We have found that no one treatment program covers all the variations possible. The two 8,000 gallon equalization tanks minimize the variations but do not eliminate them.

Semi-Continuous vs. Batch Treatment: The degree of variation of wastewater characteristics led us to realize that the 2,000 gallon equalization tank we were using for semi-continuous treatment was inadequate. We were treating about 2,400 gallons per day on one shift and collecting water overnight and over weekends. About halfway through the day shift, the overnight accumulation was nearly treated and additional raw wastewater was treated directly with minimum equalization. Due to the small size of the tank, we did not have the luxury of isolating it for treatment. We made the decision to treat only isolated batches. By isolated I mean that we cut off flow to one of the two tanks and treat from it while the other collects water. This has advantages and disadvantages. The main advantage is that the variability of wastewater is at least controlled during the treatment of the batch. We run a jar test on the feed water before the batch treatment to establish the exact dose of chemicals we need. However, the disadvantage of this scheme is that the DAF operates in eight hour periods when DAFs are best utilized continuously. We have learned to overcome this disadvantage with self-taught operational skills.

DAF Stabilization: The key to stabilizing the DAF during a short operating period after having been stagnant for a longer period is to start chemical flows about one-half hour before starting wastewater flows. The second major operational secret is to pay attention to the pH in the DAF itself. To this end, we installed a second neutralization step just prior to the DAF to optimize the pH. Thirdly, we made a mechanical change in the recycle system to achieve better balancing of air and water. With these three changes, we successfully operate the DAF batchwise.

Bacterial Activity: One lingering problem area under investigation is the presence of anaerobic bacteria in the system. Especially in the summer this becomes a smelly problem but, worse, it adds to the sludge generated and even overcomes the effective capacity of the DAF. I have estimated as much as 30% sludge in the DAF, about ten times normal. We take steps to kill bacterial activity as soon as spotted but even dead colonies create a thick sludge. All ineffective treatments have been linked to unusual volumes of sludge generation.

Major Maintenance Problems

Besides learning to operate the oily wastewater plant, the maintenance is very critical because oily wastewater is tough on equipment.

Pump Clogging: One problem is frequent clogging of front end pumps. The addition of an oil-water gravity separator and two 8,000 gallon equalization tanks provide most solids and debris a chance to settle out before the pumps, but strainers are still required. Even so, we have a requirement to disassemble, clean, inspect, and reassemble all front end centrifugal pumps on a monthly basis.

Media Clogging: When the DAF operates inefficiently, a large volume of solids carries over and is trapped in the media filters. This situation cannot go uncorrected for long, however, because the media clogs up and needs to be changed. Our main efforts have been aimed at more efficient DAF operation and better chemical removal of oil and other solids.

Oil/Rubber Incompatibility: The media filter bank was fabricated with direct air-operated rubber diaphragm valves, but these proved to be a constant source of headaches until we replaced all these valves with indirect operated metal diaphragm valves. After 18 months with the new valves, we have had no malfunctions.

Conclusion

Some designers maintain that effective heavy metal ion removal from wastewater with simultaneous oil removal is incompatible. I'll be the first to admit that it is a tough problem, but I am here to tell you that it can be done.