Interview

Removing Metals from Wastewater

A conversation with Hubbard-Hall's Robin Deal

Robin Deal has been with Hubbard-Hall for 7 years as a Field Service Engineer specializing in industrial wastewater treatment. Prior to that, she worked for a major industry as a wastewater operator, holding a physical/chemical wastewater license in the state of North Carolina. She has completed the Wastewater Treatment Plant Operations Specialist certificate program at Sacramento State University. Robin continues her education in wastewater treatment with the goal of holding a degree in Environmental Management. She currently spends her time in the field educating customers while helping them meet their wastewater permit requirements. In the lab she works toward finding efficient ways for customers to transform their wastewater treatment processes to a lean wastewater treatment process.

What is the process for chrome reduction? What chemicals does it take?

Hexavalent chrome is the positive six state. It is extremely hard to get out of wastewater, and it is also very harmful to humans because it is a carcinogen. It is in our wastewater via plating or chrome coatings, and we have to reduce it before we can remove it. So to reduce it, you want to drop your pH to 2.5 or below, and then you want to raise your ORP to +250 or above while maintaining a 2.5 pH. How you raise your ORP is by adding a reducing agent such as sodium metabisulfite, which is most commonly used. But you can also use magnesium sulfate, ferrous sulfate, or any reducing agent. There are several ways you can do it, but the key to remember is you have to be at a pH of 2.5 and a +250 ORP when you introduce the reducing agent. You will want an acid to keep your pH at 2.5 as the pH will increase as the chrome reduces, most people use sulfuric acid. Whatever chemical reducing agent you use, with the right pH and the right ORP hexavalent chrome will reduce to trivalent. A good indication is if in your stream you only have hexavalent chrome — and hexavalent chrome is yellow in color — when it is reduced, it turns to this pretty blue color, and that's how you know you succeeded.

What is the difference between a coagulant and a flocculant/polymer?

A coagulant is considered something that gathers ultrafine particles. It is the first part of any precipitation process; we put it in, and then we raise the pH, so you always put your coag in at lower pH, and then you adjust your pH to where you need it to be. What happens then is your coagulant will start

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forming hydroxide — or sulfide bonds — and you will start to see this real fine floc floating around — it is called pin floc. Coags can be aluminum, iron, calcium; any kind of metal salt is what a coagulant is. The technical definition in wastewater is something that gathers ultrafine particles together. A flocculant — or you will hear people say polymer as well — is what grabs those fine particles together. It is slimy and sticky. So much so that some people refer to it as the "snot". It gathers the pin floc together and makes larger particles or floc. Flocculants can be of three charges: they can be cationic, non-ionic, or anionic. Based on what you're trying to remove, that's how you determine which flocculant you want to use. Anionic polymers or flocculants carry negative charges, and cationic carries positive charges. So if you're trying to remove metals — and metals carry a positive charge — you tend to go with an anionic flocculant because they carry a negative charge. Organics carry negative charges, so cationic polymers will attract them.

How do you get a nickel out?

If it is solely nickel we're going after, we want to use an aluminum-based coagulant because aluminum has a high affinity for a nickel. We want to take the pH up to 10.5 or higher to pull it out. If there's any kind of chelation present — and in the plating world, there usually is some chelation — we may find that we have to use a metal precipitant such as DTC or sulfide to help break those chelation bonds. Because nickel is the highest pH metal for hydroxide precipitation, you may want to do sulfide precipitation, which precipitates out at a pH of around 8. Most people don't have just nickel however; there's usually a mixture like zinc-nickel or tin nickel. You have to balance your pH to what you want to remove. If you find that you can typically get zinc out really easily — but you struggle with nickel — you might want to take your pH up a little higher to grab more nickel. Or if you find you get your nickel out really well, but you have a hard time with your chrome, you might want to take your pH down closer to where chrome comes out. It all depends on that hydroxide or sulfide precipitation that you use. Metal removal via precipitation is totally pH dependent.

What are chelators, and why are they in my wastewater?

Chelators are chemicals that keep metals in solution. When you're plating, you have a supersaturated bath of metal; there's more metal than what would naturally be able to stay in solution. They often add another chemical to make sure the metal stays in solution so that you can plate it out; that's what a chelator is. It forms bonds with the metals so that the metals stay in solution. When you run your parts through your bath and then rinse them, you have drag out from the plating bath, which carries some of the chelators because it is part of the bath, and that's how it winds up in your wastewater. Some common chelators are EDTA, DTPA, tartaric acid and citric acid, which is a chelator that can be really hard to break in some cases. There is actually a list of over 400 chelators used in metal finishing now.

What's the best way to remove chrome?

When you reduce chrome, you just change its valence. You go from positive six to positive three, but it is still in your wastewater, and you have to remove it. When you want to remove trivalent chrome from your water — or if you're you have just

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chromium, and it is in a non-valence state, which can happen — you want to us a ferrous or ferric based coagulant and take your pH to between 8.5 and 9 for hydroxide precipitation. Ferrous or ferric has a higher affinity to chrome than the other coagulant bases. If you have other metals present, and at some facilities there is, you will want to adjust your pH to the best range for removal of all metals present.

How do you remove solids?

Solids can be in the form of dissolved or suspended. If they are dissolved solids, you can't see them; your water looks clear, and everything looks good, but they are still there. If you adjust your pH, they'll start to pop out, and you will start to see them. I have seen solutions that are really high in copper that look crystal clear at a low ph. When we adjust the pH up to about 8 it turns this beautiful blue color because all the copper starts coming out. You want to use a coag and a flocculant to pull them together and floc them out. If you don't have dissolved solids in your wastewater and you just have suspended solids, you can go through different types of filtration such as a bag filters, which have different micron sizes, or you can use a sand filter or a carbon filter. It depends on what your solids are and how you want to get them out.

What can you do to take care of a filter press?

When you get a new filter press, and it is a plate and frame filter press, the plates are in a very specific order. That's so it allows for the flow of the solids to go through properly. You want to make sure you never get your plates out of order, even if you have to number them. Some shops will spray paint edges of them so that they keep them in order; some plates will have indents on them. That's the number one thing you can do for your filter press: never take your plates out of order. The second is you never want to pressure wash your filter press. The filter cloths are like a super-strong napkin, if you want to think of them that way. They have a weave on them, so if you hit them with high-pressure water — such as a pressure washer—that weave will start to open up more and more, and then you start to get solids to come through. Instead, what you want to do is hook up what's called an "acid wash pre-coat system," and when your cloths are dirty, you want to run a very dilute acid — about 0.01% — of very weak hydrochloric acid or sulfuric acid through using the acid wash system. Let it run for about 30 minutes, it will cycle the acidic water through the filter press and back into the same tank, the weak acid will dissolve any buildup that's in the weave of the cloth. That weak acid water will need to go back into the treatment tank because it will be laden with everything that was on the filter cloths.

How can you remove zinc?

Zinc is one of those tricky metals when it comes to hydroxide precipitation. It starts coming out around 8.5, but once you get above 9.5, it'll go back into solution, and then you have to take it back up closer to 10.5 or 11 to get it back out. Zinc does really well with aluminum-based coags, but ferrous will do okay with it as well. You just want to keep an eye on your pH, and if you have any chelators present, make sure you add something to help overcome the chelation catch up.

How do you make flocculant? Can you overdose on it?

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Flocculant or polymers come in three ways: they come in a ready-to-use pre-mix that you don't have to worry about; you just hook it up and go. They come in powdered form, or they come in an emulsion which looks kind of glue. There's a carrier oil present in the emulsions, and if you let it sit long enough, you will see where the oil will separate out, and you will have a layer of oil on top of your container. When you're using emulsions, and you're making up emulsions for your system, you want to make sure that you fully mix the actual emulsion before you pour any out. The general rule of thumb is to make them up at a 0.2% or a 0.1% solution, so for every 1,000 mils, you want to add 1-2 mil to get to your 0.1%, or 0.2% mixture. You want to mix it, so you have your day tank with water going in it and then pour your mixture in while the water is going in and the blade is mixing, or you can get a polymer to make a down system for emulsions. Polydine makes a very nice one where it injects the polymer in with the water as it goes into your system and so you don't have to mix it at all; it is just the water flowing and the emulsion flocculant is automatically injected. When you make up powdered flocculants, it is the same rule of thumb: you want 8 grams per gallon of water which will make a 0.2% solution. You want to make sure your water is moving with the paddle, and you want to sprinkle your powder; you don't want to just dump it all in, or it'll clump up. The goal is to try to get every grain of powder wet before it touches another grain when it is in solution, or otherwise, you get what they call "fish eyes." "Fish eyes" can clog up pumps. They actually make a flocculant dispersion unit if you have powdered flocculant that is basically a funnel that has a water hose attached to it; you turn the water on, and then you sprinkle the dry powder on the funnel sides, and it funnels down so that it wets every grain and keeps fish eyes from happening. You can overdose flocculants, and the first sign is your effluent will start to look a little cloudy; if you touch it, it'll feel oily. If you continue to overdose — or you continue to dose higher and higher — the flocculant will start to float on top of the water, and you pretty much have to shovel off of your mix chambers where your polymers were introduced into your wastewater. Another thing that will happen is it can cause your floc to float instead of settling. That could be another problem that might let you know you might need to turn down is if your floc's floating.

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