Wastewater Treatment & Recycling Panel Provides Forum for Further Discussion Of MP&M & Other Concerns*

Each year one of the highlights of the AESF/EPA Conference for Environmental Excellence is the Wastewater Treatment & Recycle Panel. This year was no exception. The room was packed with attendees vying for a chance to ask the "world-class" panel questions ranging from operational concerns to meeting the dreaded Metal Products & Machinery (MP&M) Guidelines. Experts in wastewater and recycling disciplines, including ion exchange, reverse osmosis, chemistry, laboratory and regulatory, were present to meet the challenge. The panel boasts more than 100 years of collective experience. The opinions expressed here are those of the panelists as understood by the reporter. While it is hoped that there is value to the edited questions and answers provided, it is recommended that you conduct your own research before making changes in your system.

(Left to right) Moderator Thomas H. Martin, CEF, Delta Chemicals & Equipment, Inc., Indianapolis, IN, reads a submitted question to be answered by the "world-class" panelists: Lyle Kirman, Kinetico Engineered Systems, Newbury, OH; Jeffrey Lord, CEF, Mayer & Associates Manufacturers' Representative, Cleveland, OH; Frank Altmayer, CEF (AESF's technical director), Scientific Control Laboratories, Chicago, IL; Dr. Fred Reinhard, CH2M Hill Engineered Systems, Eagan, MN; and Julie Rogers, Rogers Consulting, Phoenix, AZ.

Metal Products & Machinery (MP&M) Rule

Question: Will there be life after the MP&M Rule? I have a cyanide (CN) flow-through conventional wastewater treatment system.

Altmayer: It is unlikely that any company plating with cyanide on steel substrates will be able to consistently comply with the cyanide limits, because they must be met at the point of treatment. Everyone knows iron cyanide complexes do not respond to alkaline chlorination, so your total cyanide after chlorination may be as high as 30-40 ppm. The cyanide-amenable to chlorination limit is 0.07pp m a o30-day average, so how can anyone analyze 30 ppm twice within 0.07 ppm? The analytical problem will give you violations, because the cyanide analysis cannot be repeated with that kind of precision, and cyanide amenable to chlorination requires two tests, where one is subtracted from the other.

It is estimated by the EPA that you will have to spend $250,000 on ultrafiltration to meet the new source MP&M limits. You may be able to employ cation exchange at a reasonable price, then you have some hope of meeting the new MP&M metals numbers. One of our members has gone this route, but still has difficulty meeting the MP&M limits, as you heard this morning. For cyanide compliance, you're going to have to go closed loop on the cyanide-bearing process. The used equipment market is quite favorable right now for buying this type of equipment to meet CN limits. You can buy vacuum-type evaporators, for example, for about 20 percent of the original cost. EPA is on the rampage for CN.

Reinhard: I would suggest taking care of things one step at a time and get in early, and not wait for the final numbers. Our members must take very seriously what is going on now.

Rogers: In the Phoenix area, we have one company in particular that has closed the loop on its hexavalent chromium (Cr^{+6}) and nickel lines while leaving cleaners on the sewer, and is still meeting stringent numbers. If you don't introduce those metals into the waste streams in the first place, you need not worry about their removal later.

Kirman: Don't give up just yet. The numbers aren't final. It is a good time to plan, but I would recommend against buying equipment now. Now, however, is the time to submit comments to the EPA.

Altmayer: Another comment on life after MP&M. According to EPA, 10–15 percent of you will go out of business. We feel, however, that it will be more likely that 30 percent or more of our industry will not survive. Many companies are investigating relocation to Mexico, Canada, Taiwan or China—where they have the impression that regulations are weakly enforced. There will be life, but not as we know it today. The new source standards are the monsters in MP&M and we'll all be new sources at some point in the future. Therefore, there are many unknowns in this regulation. If one can't reliably meet new source standards, then they may

**This report was compiled by Martha Martin, CEF, and edited by Frank Altmayer, CEF, and Sylvia Baxley.*

have to haul the concentrates away and pay for disposal at a centralized treatment facility that is allowed a discharge limit of 500 ppm CN.

Some feel zero discharge is the only way to go; however, zero discharge can present an entirely new group of problems. When the contaminants build up in a chromium solution, for example, it may be necessary to replace the plating solution every three years and haul away the contaminated solution for off-site treatment. It doesn't make a lot of sense to haul contaminants away and bury them in the ground. That doesn't really accomplish much for the environment or make a lot of sense.

Question: How do the pretreatment rules affect new discharges to the sewer?

Altmayer: The limits for a particular regulated parameter may be 0.03, 0.06 or 0.07 mg/L as a new source. Existing sources that add a new line will be considered a new source for the new line, and will therefore get the more restrictive limits. For example, in Chicago, if you change your line by adding 50-percent more capability, then the facility is reclassified as a new source. Or, in some cases, a change of 33-percent increase in process lines could result in classification as a new source. The difference in limits for a new source compared to an existing source is a factor of three to 10.

Question: Is zero discharge the only way to meet these limits?

Reinhard: Zero discharge certainly is safe. In complying, however, companies need to look to many creative solutions to reach the goal. In the case of zero discharge, one must work out the operational problems, such as impurities building up in the bath. In this case, the bath is an asset and, facing the alternative of concrete being poured into the sewer to prevent discharge, one might consider contract waste management. In the strictest sense of the word, however, any waste stream that must be contracted out is not truly zero discharge.

Question: Are many going to be able to comply without going to the extreme of zero discharge?

Reinhard: Serious attempts at zero discharge are being made; however, others try to do it in their own way. This is, after all, the American way. In America, people feel they have the freedom to reach the limits in whatever way they want. This, of course, will bring attempts at many different solutions.

Altmayer: Certainly there are plating companies finishing one or two metals that can meet the numbers. Recycling and recovery can help. Burnishing and other processes, however, make meeting the existing source limits very difficult. It must be pointed out that EPA thinks it found plants that could meet the numbers for four days. We must ask if the surveys are realistic, or is it just a "best spin"? There are human problems encountered in demonstrating an out-of-compliance situation to the EPA. The wonderful part of the system is that the EPA does listen, and we believe the EPA's data is flawed. The regulations may not come about as proposed, if enough comments and data make the EPA realize that the rule is unworkable and unjustifiable. Tin, molybdenum and manganese do not belong in this regulation. The cyanide limits must be realistic and reflect what alkaline chlorination can actually accomplish on complexed waste streams.

Rogers: I might add that there is serious opposition at the local level of Publicly Owned Treatment Works (POTW) to the MP&M. Our regulators predict that their workloads will double right at the outset.

Question: I feel the zinc (Zn) numbers didn't come from a plater. My question is, can 90 percent of shops meet the Zn limits?

Lord: No one here can guarantee that you can meet the numbers. I would urge you to look at your processes and understand them better, and improve loading along with polishing in some way. Of utmost importance is the segregation of waste streams in order to treat them individually. Look at the process and treat the analyte at the source whenever possible. It may be desirable to close the loop in some cases, decrease water usage by as much as 90 percent, and explore recovery solutions. For jobshops with a diverse chemical makeup, it may not be in the cards to meet the numbers on Zn at 0.55 mg/L and, as a new source, 0.17 mg/L for 30-day average.

One other important point to consider: the permits required to operate a "totally closed-loop" system. A totally closed-loop system could have negative consequences. For example, a shop could be reclassified as a recycle facility or a Resource Conservation & Recovery Act (RCRA) Part B Treatment Storage Disposal Facility (TSDF) because of storage of hazardous waste. Therefore, don't get the impression that zero discharge is a tidy solution.

Question: Is it important to always be able to discharge?

Martin: Permits are issued for three to five years, generally speaking. If you do not discharge any water, you can always check "No Discharge" on the monthly report of operations, but still have the option of discharging, if required. You can be in legal limbo if the permit is lost. I understand that getting an RCRA Part B permit can cost $300,000 and take three to five years to obtain.

Question: What about sulfide levels with dimethyldithiocarbamate (DTC) and sulfide as a compliance issue?

Kirman: Many cities have banned DTC, which is a biocide, because of incidents at POTWs. It is frequently used to treat organic matter that becomes biologically active in holding tanks. It is reactive and could explode. DTC is not Best Available Technology (BAT).

Martin: With respect to DTC, sulfides are harder to handle than hydroxide precipitates. Without DTC, some plants cannot meet the discharge limits. A case that cast doubt on DTC was the Indiana White River fish kill. In that incident, DTC apparently killed the bacteria in the municipal plant that breaks down ammonia in raw sewage. The resultant release of ammonia into the stream was far above the effluent limit of three ppm. At 4-5 ppm, nitrogen as ammonia will kill fish.

Lord: A manufacturer of DTC has developed a probe to read the concentration of DTC. It is designed to shut off the DTC and thereby avoid an excess that could result in a shock load. Back to the Indiana fish kill:

There were other analytes that were suspect in the fish kill, including Ni, Cu, Cr^{+6} and formaldehyde.

Question: I do zinc phosphatizing, as well as zinc and cyanide copper plating. Will an additional clarifier meet MP&M numbers?

Altmayer: Heavy coagulation with iron chloride and lime neutralization can get low metals numbers, but generate a lot more sludge. You'll make 30-percent more sludge by using lime because you make gypsum (calcium sulfate).

To get to the proposed low-cyanide numbers, however, it must be closed loop.

Question: Some suppliers recommend nano- or ultrafiltration for recycling cleaners. What are your thoughts on this?

Altmayer: A lab study is required to simulate the treatment, and that will tell you if the technology will work. Some suppliers offer loaned equipment for trials. You might also take a look at the new biological cleaners that use "microorganisms" to eat the oil.

Question: How do we achieve zinc and nickel numbers in MP&M?

Altmayer: The proposed zinc limit for an existing shop is 0.17 mg/L and for a new facility is 0.06 (both 30-day averages). The proposed 30-day average nickel limits are 0.64 for an existing facility and 0.75 for a new facility. At first I thought the higher nickel for a new facility was a "typo," but EPA has confirmed that its database for new facilities was limited and resulted in a higher set of numbers. How that can be justified is hard for me to understand. Certainly, at a minimum, an existing facility should be allowed to meet the higher new-facility nickel number, but more likely, EPA should take a better look at its database, and resolve this dichotomy.

Anyway, back to your question, to consistently meet the new source numbers for zinc, you'll need to employ closed-loop recovery. The existing source zinc and both nickel numbers may be met with conventional precipitation, followed by polishing filtration, followed by cationic ion exchange.

Cation Polishing & MP&M

Question: I have low pH and high TDS and cationic regeneration doesn't help. What is wrong? We have both cation and anion beds.

Reinhard: You have a problem with your anion exchangers. A correctly functioning cation-anion exchange resin reduces TDS and lowers pH. You may have oxidizing agents present. Bleach converts gel-type anion exchange resins to a cation resin, so you have a non-functioning anion exchange resin in your ion exchange system.

Question: Can we meet MP&M with cation polishing? If so, what kind of media would you use for a polishing filter and ion exchange?

Kirman: Pretreat the water prior to ion exchange. Amminoacetate resin will not work in the presence of EDTA. If amminoacetate doesn't work, you get into expensive problems—usually a chelator problem upstream.

Reinhard: We pretreat to prepare water for ion exchange. Testing doesn't guarantee that problems won't happen, however. Evaluate the charge load in the water. If you decide to recover the water, then polishing is all that is left. Record the loading in terms of salt to the system. Increasing TDS and increasing impurities equals an increasing load on the system. What we are talking about is chemistry and ion equivalents per volume units/liter. So when I'm looking back 20-30 years, five milligram equivalent/liter = 100-200 mg/L of dissolved solids was an economical threshold for ion exchange systems.

Kirman: To put it into the context of cost and quality, you must look at why you are recycling water. Look around the country at the cost of water. As one pays more dollars per thousand gallons of water, the rules change. If you have greater than 500 TDS calcium carbonate, you may want to use membrane or ion exchange.

Rogers: EDTA complexors can mess up ion exchange.

Question: What kind of total organic carbon (TOC) numbers will you see?

Altmayer: TOC indirectly measures the amount of organic matter in the effluent. Any compound containing the element carbon, including cyanide, contributes to the TOC reading. This includes wetting agents, brighteners, grain refiners, and most all other additives in your metal finishing processes.

The only readings for TOC on a metal finishing effluent that I can remember were from the Savannah River Plant. We did a project there that came up with TOC readings of about 1000 ppm, if I remember correctly. The EPA proposed limit is 59 ppm on a 30-day average.

You'll want to prepare a Toxic Organic Management Plan (TOMP) so you don't have to monitor for TOC. EPA threw in a requirement in the TOMP that you somehow monitor and control excess chlorine in the cyanide treatment discharge to limit formation of halogenated hydrocarbons. How you are supposed to do that and also meet the cyanide limits is something nobody really knows at this time.

Carbamates & Other Problems

Question: Why did EPA include DTC in its Best Achievable Technology (BAT) and then put in a sulfide limit. How does this make sense?

Altmayer: EPA did not include the use of DTC (dithiocarbamates) in Option 2. Use of DTC is not BAT. EPA is concerned on how to manage DTC in facilities, and is seeking comments and suggestions. Based on these comments, they could ban or limit the use of DTC. DTC is absolutely crucial to some facilities in meeting the existing discharge limits. It is a wonderful product for breaking chelated metal complexes and allowing separation via clarification. DTC or some variation of this compound is often "hidden" as an ingredient in some flocculation agents or coagulants.

Question: Why are (Sn) manganese (Mn) and molybdenum (Mo) in MP&M and where do the latter two come from?

Altmayer: You'll find molybedenum and manganese as alloying elements in steel, stainless steel, and other metal alloys. When you pickle or passivate these metals, the alloying elements become dissolved in the

process solution and enter the wastewater stream. Our experience with molybdenum is that you cannot remove it by pH neutralization and clarification. We tried all pH values without success. You might give it a shot with electrocoagulation. We have no data on manganese and tin appears to be amenable to precipitation with a lot of coagulation, but I also have experienced colloids of tin that did not settle well at all.

The MP&M regulations claim to save the environment from a total of 1.7 million pounds of "pollutant equivalents." One million pounds of that is CN; 250,000 pounds is Sn; and 148,000 pounds is Cu. With tin being of the second-highest benefit, you can quickly see why EPA put tin into the regulations, because the environmental benefit of the regulation drops significantly without tin. The problem for industry is that there is no legitimate reason to regulate tin. Tin has not been regulated since the Clean Water Act was passed, and EPA made no indication of regulating tin in all the public hearings held last year. Yet it "magically" appeared in the proposed regulations. Something is terribly wrong here.

Kirman: It is a phantom number on Mo. It was news to the EPA that Mo doesn't precipitate. We want to see the plant that had it in the inflow and it wasn't in the outflow.

Altmayer: EPA took out the iron (Fe) and aluminum (Al) and just put other metals in—that's inexcusable. The justification is the same as what it used for the iron and aluminum they took out. They are using these three metals as "indicators" of a well-operated system. The reality is that a well-operated system needs no indicators, because the metals will be at concentrations the technology can achieve.

Rogers: I attended an EPA presentation in Washington, DC last September where EPA tried to tell us that we platers are chemical manufacturers because of valance changes during electrolysis, and that we need to report all those fleeting chemical presences on Form Rs. I am seeing more and more regulation based in "bad science." The MP&M is another arena where a lack of understanding has carried itself forward until a law was promulgated.

Question: What about boron (B), which EPA claims will be removed from the environment by MP&M?

Altmayer: You can't get boron out either, because it won't precipitate. EPA claims that a large amount of boron will be removed from POTW inflows by the treatment requirements of MP&M. Boron is not removed by Option 2, however. We had a boron limit enforced in Chicago in the early '70s and found there was no way to get it out of the wastewater. We ended up showing the regulators that, geologically, the Illinois area is boron-deficient. As far as I know, the regulation is still on the books, but is no longer enforced.

Reinhard: There is a way to potentially get boron out. Segregate the waste stream, use membrane technology, electrodeionization and the resultant liquid boron waste can be disposed of.

Rogers: One can always question that boron silicate glass bottles may be leaching out boron into the sample.

Recovery Systems

Question: Is silver (Ag) cyanide (CN) closed loop for silver recovery a good idea?

Kirman: Vacuum evaporation is used for AgCN, but impurities build up over time. Deionized (DI) water is essential. Precipitate the carbonates with barium (Ba) and route the bath to an electrowinning system, plate it out and destroy the CN.

Altmayer: Adding a chilling coil to lower the temperature to 65° F will slow down the build-up of carbonates, but you need to determine if that operating temperature has an effect on the appearance of bright deposits.

Question: Where would a reverse osmosis (RO) unit best be used? Nickel rinsewater, copper cyanide rinsewater or well water?

Kirman: A reverse osmosis unit works best on incoming well water. When used on nickel, boric acid rejection is poor, because it goes through the membrane as an impurity. For cyanide, reverse osmosis is almost impossible because of high pH. One ppm calcium (Ca) at a pH of 10.5 will foul the membranes. The pH to ionize CN is very high. Therefore, well water is the best application of those mentioned.

Altmayer: RO is best applied to produce usable water from well water. It is applicable to nickel plating solutions, but you might need to go to advanced reverse osmosis to concentrate the rejectate, as the basic RO typically delivers a very dilute rejectate that needs further concentration via evaporation. When recovering nickel plating solution, there are solution growth problems. Nickel anodes dissolve at 100 percent, while Ni cathodes plate at 85-95 percent. One plater had the nickel salts build up so high they crystallized out on the walls of the tank, and gave him roughness trouble.

Reinhard: The key is pretreating the well water with RO. Calcium hardness must be accounted for before RO. This can be very touchy. This is a complex problem and you will need to investigate a lot of pretreatment techniques. I agree that hauling away concentrated waste streams is a good solution.

Laboratory Analyses

Question: My copper and zinc analyses that the POTW did are 10 times higher than my outside contract lab. I have requested that the POTW split the results and take my additional analyses to average, but they won't listen and will not discard their higher numbers. I have now received a Notice of Violation (NOV). How can I deal with this?

Altmayer: It sounds like you are not on a first-name basis with your regulators. You have legal recourse, and, as a last resort, can sue them and a judge may force them to accept your data. Or, you could go to your EPA Regional office and ask for an interpretation. You can make it known that you have legal recourse. In all your sampling and gathering of data, be certain you use certified laboratories, follow proper sampling protocol and use chain of custody so your data can be accepted in court.

Lord: There can be differences between split samples analyses. Improper sampling techniques can result in variation.

Question: I have a problem meeting my cyanide numbers. I get poor

results from different labs on the same sample.

Altmayer: The cyanide test doesn't work well if you have a complex matrix of sulfides and organic matter. There are several methods for analyzing CN, including standard methods, EPA methods, and ASTM methods. The cyanide amenable to chlorination test is a joke. It will make you self-report violations that do not exist. The test is difficult to reproduce. The Weak Acid Dissociable (WAD) test is more reliable for free cyanide. At least one discharger has obtained approval of ion chromatography for cyanide monitoring, because this method is not subject to sulfide interference.

What to Do In Case of a Spill

Question: I had a spill in which a release of sulfuric acid in a reportable quantity (RQ) left my facility. The spill went down the street to the storm drain. I tried to respond to the spill, but the regulatory police came. Do I have any way out of this mess?

Altmayer: If there was no criminal intent on your part, it should be construed as an accidental spill. Call your attorney.

Rogers: It is important to report a spill right away. In our area, one call to 911 will generally get all the notifications started. It's better to call them because they have real concerns for public safety. Keep in mind, however, that they tend to overreact. The environmental police are just part of the process. Call them right away, because they are really there to help you. If you delay in calling them, however, they become "the cops." Your way out of this mess is to admit your spill occurred because of whatever reason, then show the steps taken to prevent another occurrence. More training, better equipment, whatever it takes. They don't want to put you out of business.

Lord: There should be detailed instructions in your Emergency Contingency Plan that outline when and whom you must call. Be advised that if you have a spill, afterwards you must revise your plan to address how to prevent another such spill from occurring. The plan also addresses training provisions, notification to the fire department, police, hospital and local emergency planning agency. If you followed your plan, you should have done what you need to do.

Question: What is "immediate" notice?

Rogers: Call in seven to 10 minutes. The National Response Guide says immediate is 15 minutes.

Miscellaneous Concerns

Question: My wastestream is 80-percent oil and 20-percent water. Is there a splitting technology for oil and water?

Martin: One of my clients is a large automotive transmission plant. The have a "cooking" process to get out water. They add 1–2 percent of concentrated sulfuric acid, raise the temperature to 290° F. and let it cool overnight. You will get three layers. The top is oil with only 2–3 percent water, the middle is "rag" and the bottom is water. Generally, to burn in a boiler, it should only have 2–3 percent water. The surplus oil they cannot use in-house is sold on the open market.

Question: How can I improve operating cost on reducing Cr^{+6} to Cr^{+3}?

Lord: With Cr^{+6}, go to the process and recover. Close the loop and eliminate hexavalent chromium from wastewater treatment.

Question: Is there a process to remove Cd from Cr^{+6} chromating solution?

Lord: In aerospace applications, membrane and recycle will remove it.

Final Comments on MP&M

Question. Would you suggest we act now and invest in new wastewater treatment technology, or should we wait?

Altmayer: We would recommend not investing in new equipment just yet. There is hope that we can change the regulations. I am convinced the regulations are based on faulty conclusions.

We have a very short window in which to submit comments to the EPA. They are looking for at least four influent data points and four effluent data points. The sampling protocol must be proper and a certified laboratory must be used for analysis in order for the data to be accepted. EPA wants "matched pair" data. That means influent and effluent analysis. The deadline for submission is just around the corner.

Closing Comment from A Former EPA Official

I am a retired EPA official who used to write regulations. Now I am a professor at a college here in Florida. I want to thank the panel for your advice to the attendees. It has been good advice, but there is one important thing no one has told you.

You do need to comment and sample, just as Mr. Altmayer has said; however, if the rule will cost you $250,000 or more to comply with, then you need to tell the EPA how that will impact your operations. If it will make your business unprofitable, then say so.

The rule-makers are technical writers and the economic impact is often lost on them. They can analyze your raw data, but it's hard to explain in-house the economic impact of the regulations on business.

EPA feels that you can pay for the cost of the equipment to meet the regulations with a price increase to your customers, but I have talked to many companies that have received price concession letters from their customers. They cannot pass the cost on to the customer.

EPA feels that anyone can meet the numbers, but you are now competing on a worldwide basis. You may lose your business to competition from China, Taiwan, Mexico and Canada. This is what you need to tell the EPA, in addition to your raw sampling data. If this is true for you, then please address it in your comments. *P&SF*