Treatment of Metals Finishing Wastewaters from the Aerospace Industry

G. Dave Manku, P.Eng., Dr. Stephen R. Harper, P.E., & Randall C. Shaw, P.E.
Brown and Caldwell, Atlanta, Georgia

Abstract
Aerospace industry (AI) wastewaters typically contain elevated concentrations of a variety of metals held in solution by chelating agents. AI wastewaters tend to be highly variable, with metal concentrations ranging between 10 to 1,000 mg/L along with contaminants such as oil and grease, COD and surfactants. Wide ranges of chelated and unchelated metals concentrations are also common and the effects of chelants were investigated here by comparing treatment performances of some proprietary chemicals versus traditional hydroxide precipitation. Based on the treatability tests performed, chelated metals removal on the order of 90% (or better) was achieved using novel precipitants. Results from treatability studies conducted at two metal plating shops within the aerospace industry are presented. Performance was compared based on percent metals removal of certain metals including Cr, Cd, Ni, and Pb. The impact of chelating agents on treatment performance is discussed relative to the various treatment chemicals tested. Corroborating results using other wastewaters and other chelants is provided.

For more information, contact:
Dave Manku
Brown and Caldwell
41 Perimeter Center East, Suite 400
Atlanta, Georgia 30346-1905

Introduction

The aerospace industry generates wastewater during the routine washing, repair and maintenance of aircraft and aircraft parts (engines, bodies, landing gear, bearings, brakes, etc.). The wastewaters generated tend to be either highly basic or acidic and typically contain elevated concentrations of metals such as chromium, cadmium, nickel, and lead as well as oils and greases, cyanide, detergents and surfactants. Laboratory-scale treatability tests and full-scale process optimization tests performed at plating shops within the aerospace industry are discussed in this paper.

Conventional Treatment

The conventional treatment method for removing metals from wastewater includes adjusting the pH to the minimum solubility point of the metal. The resulting metal hydroxide precipitate is typically coagulated using alum, ferric chloride and/or organic-based polymers and removed by sedimentation. The hydroxide precipitation method can be optimized for a single metal only. For example, the lowest solubility point for cadmium is approximately 11 while that for chromium is approximately 7.5 with other metals such as Fe, Ni, Pb, and others in between. For wastewater streams containing multiple metal contaminants, the hydroxide precipitation method can be severely limited. Therefore, treatment of wastewater containing combinations of metals often requires specialized chemicals and polymers to meet discharge criteria.

Chelant Effects

Generally, the goals of the plating shop and the wastewater treatment plant (WWTP) are in conflict. The aim in plating is to maintain a metal in solution so that it may be deposited onto the surface of the work piece. Conversely, the purpose of the WWTP is to remove metals from the solution via precipitation. Thus chemicals used in the plating shop to hold metals in solution (i.e., chelating agents) have the potential to dramatically effect the performance of the wastewater treatment plant. Specific chelating/complexing agents encountered include cyanide, aqueous ammonia, and sulfamate. Other chemicals that are commonly encountered that result in process upset conditions in the WWTP include: EDTA, triethanolamine, sodium gluconate, citrus products, surfactants and detergents.

Many of the operations at plating shops tend to be batch processes separated within specialized treatment and inspection areas, and the wastewater generated at these locations tends to be highly variable. The high degree of variability in the influent wastewater characteristics makes the operation and control of the WWTP extremely challenging.

Preliminary Process/Operational Considerations

To reduce potential for process upsets arising from variations in influent wastewater characteristics, a number of operating strategies can be adopted. The first strategy would be to identify all waste streams that cannot be treated at the treatment plant. These streams should be segregated and appropriately disposed off-site. The second strategy would be to provide flow and contaminant equalization. The final approach would be at source segregation and specialized pretreatment of selected streams that might impact precipitation and coagulation. This may include segregation and oxidation of cyanide-bearing wastewater, reduction of chromium-bearing wastewater from the hexavalent to the trivalent state, or chemical treatment of wastewater containing oils and greases followed by biological treatment.

Cyanide oxidation is a two-step process that can be conducted in a single stage or two-stage process using hypochlorite. The first step results in the production of the cyanate ion at a pH value of approximately 10.5. In the second step, additional hypochlorite is used at a pH value between 8 and 8.5 to produce nitrogen and carbon dioxide.

The reduction of chromium (Cr^{+6} to Cr^{+3}) from chromate or dichromate solutions is accomplished at a pH value between 2 and 4. The reducing agent typically used is sodium meta-bisulfite.

Experimental Methods

A series of jar tests using influent wastewater from facilities were performed for each treatment chemical investigated. The metals precipitation reactions were setup to simulate full-scale operations. A series of chemical dosages were investigated to determine the optimal dose for each precipitating chemical of interest. The precipitating chemicals tested include: sodium hydroxide, two DTC-based precipitants and one non-DTC-based proprietary precipitant. Prior to conducting the precipitation reactions, the cyanide oxidation and chromium reduction steps were conducted as needed.

Results and Discussion

The treatment plant at Site A processes approximately 130 m^3/d (35,000 gpd) of plating wastewater. Prior to metals precipitation in a continuous process, the cyanide-bearing wastewater is oxidized and the chromium-bearing wastewater is reduced. The pH of combined wastewater is adjusted to approximately 9.5 and the solids removed. Dithiocarbamate (DTC) based metal scavenging polymer (MSP) is used to remove the remaining soluble metals. The wastewater is filtered and tested prior to being discharged to the city's sewage system.

Site A

Preliminary test results and operating data from the plant indicated that under normal operating conditions, effective metals removal can be achieved using the hydroxide method alone. This is due mainly to the fact that influent wastewater contains low concentrations of metals and the metals are not complexed. However, periodic process upset conditions cannot be treated with conventional hydroxide precipitation due to either high metal concentration or the presence of chelating agents.

Table 1 shows the typical metals concentrations in the influent wastewater, the concentration during a process upset and typical discharge limits. The results of the hydroxide precipitation tests are shown in Table 2.

Table 1. Summary of Typical Wastewater Characteristics and Discharge Criteria.

	Metal Concentration (mg/L)			
Wastewater	**Cd**	**Cr**	**Ni**	**Pb**
Typical Discharge Limits	0.09	2.25	1.79	0.116
Raw (Typical)	0.06	0.30	0.04	-
Raw (Process Upset)	220	156	220	0.39

The results in Table 2 show that hydroxide precipitation alone does not provide sufficient treatment if the metals are chelated. Even though significant Cd (84%) and Cr (>99%) removals are achieved, additional treatment is required to meet discharge criteria. Chelating agents present in the test waters included sulfamate, cyanide and aqueous ammonia. The results also highlight the basic challenge to the hydroxide method. That is, for a waste stream containing multiple metals, optimum removal for each metal would be achieved at different pH values. For example, the results indicate that the optimum pH (based on metals removal) for Cd is greater than 12 and for Cr the pH is 10.5. Essentially no change in the Ni concentration was observed with the hydroxide precipitation method. Additional tests using the proprietary chemicals were performed to break the Ni-sulfamate and Cd cyanide bond, respectively.

Table 2. Summary of Metal Hydroxide Precipitation Results Using Cyanide and Sulfamate Chelated Metal Wastewaters

	Metal Concentration (mg/L)			
Solution pH	**Cd**	**Cr**	**Ni**	**Pb**
Raw	220	156	220	0.39
9	89	16.8	223	<DL
9.5	72	5.5	213	<DL
10	66	5.1	221	<DL
10.5	48	0.6	205	<DL
11	44	2.5	206	<DL
12	28	1.5	199	<DL

To simulate full-scale operation, further treatment using metals polishing chemicals was evaluated using the hydroxide treated supernatant at a pH of 9.5. Four combinations of proprietary MSPs and sulfide were evaluated and the results are summarized in Table 3. The results show that performance of sulfide and the DTC-based MSPs is similar with respect to Cr, Pb and the Cd-cyanide complex. Both of the DTC-based precipitants and sulfide, however, were ineffective against the Ni-sulfamate complex. Precipitants #3 were capable of breaking the Ni-chelant bond and dramatically reducing soluble Ni concentration. In addition, the toxicity associated with DTC-based MSPs does not exist with precipitants #3. However, precipitants #3 are early in their proprietary development and additional full-scale tests are required to validate performance.

Table 3. Summary of Metals Precipitation Results Using Cyanide, Sulfamate and Aqueous Ammonia Chelated Metal Wastewaters

WW Solution	Metal Concentration (mg/L)			
	Cd	**Cr**	**Ni**	**Pb**
Raw	220	156	220	0.39
Sulfide	<DL	0.79	213	0.04
DTC-Precipitants #1	<DL	3.63	168	<DL
DTC-Precipitants #2	<DL	3.75	165	<DL
Precipitants #3	3.95	2.26	2.18	0.3

<DL: Less than detection limit.

These results show that some metal-chelant interactions are susceptible to attack by the metal scavenging polymers. However, the appropriate precipitant and dose rate needs to be determined on a case-by-case basis.

Site B

The treatment plant at Site B processes approximately 100 m3/d (26,400 gpd) of plating wastewater. The wastewater treatment plant provides batch cyanide oxidation, continuous reduction of chromium bearing waste streams and continuous metals hydroxide precipitation using ferric chloride as a coagulant. This site has had occasional problems with elevated effluent nickel concentrations. Other effluent metals concentrations are typically below discharge criteria after metals treatment. Typical influent nickel concentrations for the period between January and August 2000 are shown in Figure 1. The figure illustrates the large variation in the nickel concentration typical of metal plating wastewater.

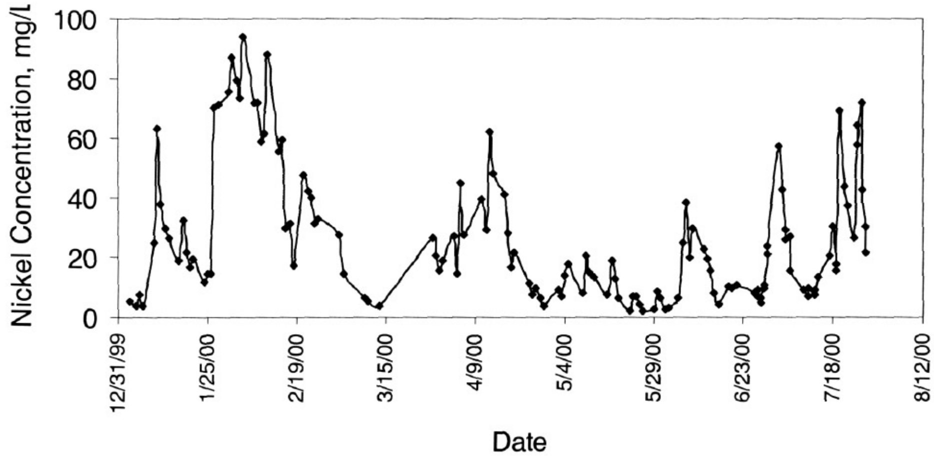

Figure 1. Influent Nickel Concentration, Site B

Based on treatability testing conducted at the site, a treatment scheme was developed to address periodic spikes in nickel concentration. Conventional treatment does not provide sufficient treatment during these process upset events. Treatment includes the use of a DTC-based metal scavenger. Due to the toxicity associated with DTC, the plant is operated at low DTC concentrations. During a process upset condition, the DTC dose is increased until the metals concentration is brought under control. The operating results from the plant are shown in Figure 2. Points of increased DTC addition are also shown on Figure 2. Figure 3 shows the increased metals removal achieved as a result of using the DTC based precipitants. Prior to December 1999, DTC was not used and the average effluent nickel concentrations were approximately 1.5 mg/L. Following implementation of the DTC-based precipitants, the average effluent nickel concentration has been reduced to approximately 0.3 mg/L.

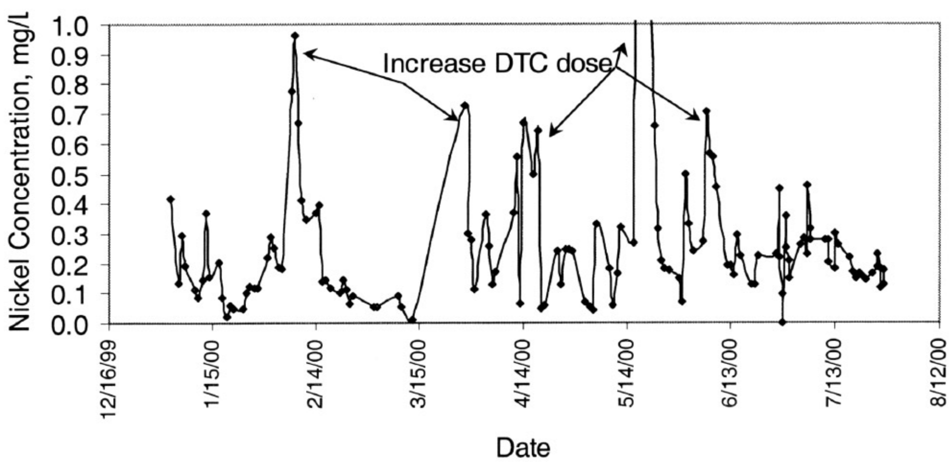

Figure 2. Treated Nickel Concentrations, Site B.

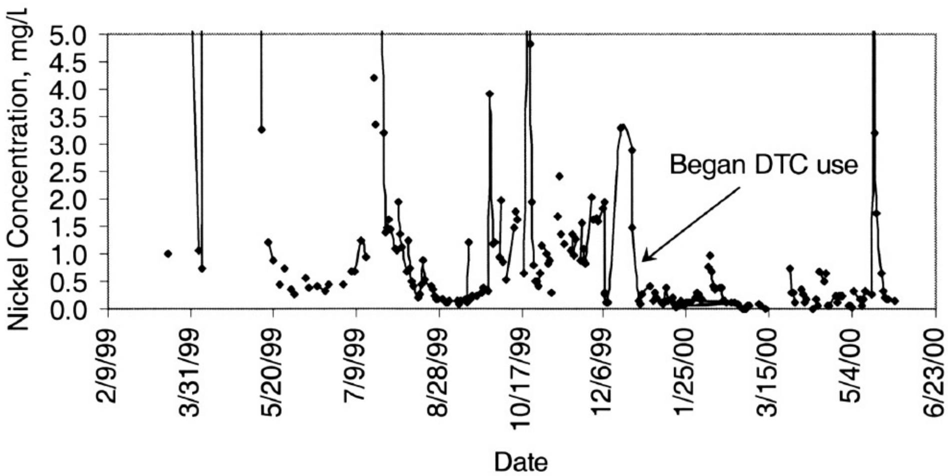

Figure 3. Impact of DTC Use on Treated Nickel Concentrations, Site B.

Conclusions/Recommendations

Based on recent experience at several plating shops, wastewater containing soluble metals can be effectively removed using hydroxide precipitation, if chelating agents are not present. However, if chelating agents are present, proprietary chemicals are required to meet discharge criteria. Several types of flocculant/coagulant chemicals were tested. The best results were obtained from DTC-based precipitants. A non-DTC-based precipitant also showed promise; however, is in early development and more performance testing is required.

Based on the testing performed, the following general conclusions can be drawn:

- Sulfide and all of the proprietary chemicals tested were capable of breaking the Cd-cyanide bond.
- Both sulfide and the DTC-based precipitants were ineffective against the Ni-sulfamate complex.
- Precipitants #3 were the only precipitants tested that effectively reduced soluble nickel concentrations when present as Ni-sulfamate.
- Hydroxide is effective, and generally less expensive than the proprietary chemicals, for treating wastewater containing non-chelated metals.