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A PROCESS FOR TREATMENT OF MIXED WASTE CONTAINING CHEMICAL PLATING WASTES

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ABSTRACT
The Waste Treatment and Minimization Group at Los Alamos National Laboratory has designed and will be constructing a transportable treatment system to treat low-level radioactive mixed waste generated during plating operations. The chemical and plating waste treatment system is composed of two modules with six submodules, which can be trucked to user sites to treat a wide variety of aqueous waste solutions. The process is designed to remove the hazardous components from the waste stream, generating chemically benign, disposable liquids and solids with low level radioactivity.

The chemical and plating waste treatment system is designed as a multifunctional process capable of treating several different types of wastes. At this time, the unit has been the designated treatment process for these wastes:

- destruction of free cyanide and metal-cyanide complexes from spent plating solutions;
- destruction of ammonia in solution from spent plating solutions;
- reduction of Cr$^{VI}$ to Cr$^{III}$ from spent plating solutions, precipitation, solids separation, and immobilization;
- heavy metal precipitation from spent plating solutions, solids separation, and immobilization, and
- acid or base neutralization from unspecified solutions.

TRANSPORTABLE TREATMENT SYSTEM CONCEPT
The treatment system for chemical and plating waste is intended to remove the hazardous components from aqueous waste solutions at numerous Department of Energy (DOE) sites. The system is designed as several transportable modules that will be connected to form an integrated skid. This arrangement allows the skid to be moved to various locations. The total area required for the treatment skid is about 10 feet by 20 feet. The skid is also designed with an auxiliary secondary containment pan that is 12 feet by 24 feet, allowing it to be permitted as a mobile treatment unit. The modules can be transported, interconnected, and mated to utilities at any site meeting the process and safety requirements.

The treatment system uses Best Demonstrated Available Technology (BDAT) processes approved by the Environmental Protection Agency (EPA) for electroplating wastes. These waste solutions are considered to be in one of three forms.

1. Listed wastes—These wastes are "listed" by the EPA as specifically hazardous wastes requiring specific handling. Special rules drive their treatment and disposal.
2. Characteristic wastes—These wastes possess one of several characteristics considered by the EPA as "hazardous." These characteristics include corrosivity, reactivity, flammability, and toxicity.
3. Mixed wastes—These wastes have either a listed or characteristic hazardous component plus a radioactive component.

Typical waste solutions requiring treatment are cyanide plating wastes, chromic acid plating wastes, metals plating wastes and ammonia-bearing plating wastes, or solutions with similar compositions. Any of these wastes may be considered mixed wastes if depleted uranium is present.
The general treatment process consists of reacting the waste solution with a variety of chemical reagents to convert the hazardous component into harmless byproducts or immobilized solid material. The treatment of choice and the order of treatment depends on the analysis of the solution mixture. Cyanide, for example, will be decomposed into nitrogen and calcium carbonate. Chromic acid is first reduced to chromous acid and then solidified as a hydroxide. Any liquid effluent is either low enough in hazardous components to be directly discharged or will require further treatment for removal of radioactivity. Figure 1 shows the treatment system for chemical and plating waste with all of the modules connected.

Figure 1. Conceptual Design of the Chemical Plating Waste System.
Module dimensions and weights are confined to 4000 pounds per module and maximum dimensions of 5 feet wide x 10 feet long x 12 feet high. The structural system is designed so that it may be easily cleaned before storage. This requirement necessitates welded stainless steel construction that greatly minimizes cracks, crevices, and corrosion products such as rust. When stainless construction is not possible, epoxy painting for nonstainless metal parts has been specified. Easy access has been provided to the internal and external surfaces of the equipment for easy cleaning and inspection.

Several safety features are designed into the treatment system. Interlocking and manual valve actuation makes accidental release of cyanide or sulfide gases into the operating area unlikely. Further, monitoring and control devices in the process, vent streams, and operating areas provide adequate safety of operation. Operation parameters are controlled to eliminate the possibility of cyanide or sulfide gas evolution by maintaining pH and concentration levels during treatment.

The modules contain the following equipment.

- The reactor module contains the reactor and a containment pad.
- Module 1 has two submodules.
  1. Module 1A contains the filter press and the upper deck eyewash station.
  2. Module 1B contains the filter drop chute, the transfer and circulation pump, and the computer control equipment.
- Module 2 has 4 submodules.
  3. Module 2A contains the dry chemical feeder.
  4. Module 2B contains the reactor and scrubber heat exchangers and the circulating pump.
  5. Module 2C is a platform for maintenance access to Module 2A.
  6. Module 2D contains the scrubber, the scrubber pump, nitrogen bottles and the lower level eyewash station.
- The utility skid contains the chiller, its circulating pump, the heater and its circulating pump, and blower. The utility skid is outside the processing skid area.
- The scales, mixer, and HEPA filters are outside the skid boundaries but within the room containing the treatment skid.

**PROCESS DESCRIPTION**

The treatment process for chemical and plating waste is designed around a jacketed, 500-gallon agitated reactor with a 60-mil Kynar® liner. An air-operated diaphragm pump charges the reactor with the waste; circulates the reaction products through a loop containing pH and oxidation-reduction potential probes to monitor reaction progress; and discharges the reactor contents through a plate and frame filter. Various connections to the vessel allow adding solid and liquid chemicals and venting. The vent line off-gases are scrubbed with a caustic solution in a venturi scrubber before passing through high-efficiency particulate air (HEPA) filters to the stack. Cooling water or heating water may be applied to the reactor jacket as needed using an intermediate heat-transfer loop. An intermediate loop is needed to prevent contamination by ensuring that the main heating and cooling system are isolated. Figure 2 is a process overview showing the components of the treatment process for chemical and plating waste.

The waste solutions must be properly identified to determine the treatment or treatments to be employed. An ICP scan of the contents will give a qualitative and semiquantitative understanding of the materials present. Analysis of the hazardous waste may also indicate the presence of an organic phase that may require further treatment of the solution.
Because several of the candidate waste streams may be in small quantities that cannot be treated in the 500-gallon reactor, the hazardous waste solutions may be blended. Administrative controls must address potentially incompatible wastes and the consequences that may arise if incompatibility is ignored.

Figure 2. Chemical Plating Waste Treatment Process Overview

Figure 3 shows a flow sequence for processing any potential candidate waste stream. One or all of these waste solutions will be likely mixed in the storage containers. Typically, the wastes requiring multiple steps will follow the order listed above to minimize formation of hazardous gas or to ensure maximum treatment effectiveness. The total volume of waste treated for each batch run depends on waste concentration and the volume of reagents necessary to process the waste.

The skid-mounted process system is designed with maximum flexibility to treat as dilute or as concentrated a solution as can be reasonably foreseen. This flexibility is especially important in the specifications for the solid-liquid separation equipment, especially the filter, because varying compositions and amounts of hydroxide and sulfide precipitates must be handled; it is also important in the specifications for reagent transfer and metering pumps. The extremes of the plating waste feed have been defined, and a unique process flow diagram and material balances have been developed for each waste type based on these extremes.

PROCESS ALTERNATIVES FOR THE WASTE STREAMS

The chemical plating waste system is designed for five main waste types:

- destruction of free cyanide and metal-cyanide complexes;
- destruction of ammonia in solution;
- reduction of Cr\(^{VI}\) to Cr\(^{III}\), precipitation, solids separation, and immobilization;
- precipitation of heavy metals, solids separation, and immobilization; and
- neutralization of acid or base solutions.

One or all of these treatment processes must be employed, depending on the waste material. Typically the wastes requiring multiple steps will follow the order listed to minimize hazardous gas formation or to ensure maximum treatment. The total volume of waste treated for each batch depends on waste concentration and the volume of reagents necessary to process the waste.
Destruction of Cyanide and its Complexes by Alkaline Chlorination

Hazardous waste materials considered for batch treatment must be analyzed for free cyanide and total cyanide. If total cyanide is present in concentrations above the groundwater standard of 0.2 mg/L, cyanide destruction treatment must be done. The cyanide radical is stable in a reducing environment and must be kept at a basic pH to prevent formation of hydrogen cyanide, a gas lethal in small concentrations.

Oxidation of cyanide waste by sodium or calcium hypochlorite is a standard process and is done in many plants treating waste cyanide solutions. This process can achieve efficiencies of at least 99% and is the preferred method of treatment. Advantages of hypochlorite oxidation for treating process effluents are operation at ambient temperature (except for complexed cyanides), suitability for automatic control, and low cost. Because alkaline chlorination is the BDAT, treatment of difficult cyanide solutions may need further procedural development. CNCl can form if the pH in the cyanide solution is allowed to drift under 10.

The advantage of using the calcium form is that the introduction of water into the reactor (sodium hypochlorite is a 12% solution) is eliminated with the solid granular calcium hypochlorite feed. Overall reactions for the processes are as follows.

\[
\begin{align*}
2\text{NaCN} + \text{Ca(OCl)}_2 & \rightarrow 2\text{NaCl} + \text{Ca(OCN)}_2 & \text{oxidize cyanide to cyanate} & (1) \\
2\text{Ca(OCN)}_2 + 3\text{Ca(OCl)}_2 + 4\text{NaOH} & \rightarrow 2\text{N}_2 + \\
& + 4\text{CaCO}_2 + 4\text{NaCl} + \text{CaCl}_2 + 2\text{H}_2\text{O} & \text{oxidize cyanate to nitrogen and carbonate} & (2) \\
2\text{Ca(OCl)}_2 + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + 2\text{CaCl}_2 & \text{reduce excess hypochlorite} & (3) \\
\text{H}_2\text{SO}_4 + 2\text{NaOH} & \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} & \text{neutralize sulfuric acid} & (4) \\
\text{Cl}_2 + 2\text{NaOH} & \rightarrow \text{NaClO} + \text{NaCl} + \text{H}_2\text{O} & \text{formation of sodium hypochlorite in scrubber} & (5)
\end{align*}
\]

Conditions are set to first oxidize cyanides to cyanates (reaction 1). Calcium hypochlorite is metered to the reactor through the dry solids feeder, as required, to maintain the oxidation-reduction potential in the range of +350 to +400 mV and temperature control in the reactor. If
needed, caustic soda is added to maintain a pH >10. Maintaining this pH level is critical to avoid the formation of toxic CNCl or HCN gas. After the conversion to cyanates, conditions are adjusted to oxidize cyanate to carbon dioxide and nitrogen. Most of the CO₂ will likely form carbonate and will not exit in the vent gas. The desirable oxidation-reduction potential and pH for this reaction are +600 mV and 8.5, respectively.

The rate for reactions (1) and (2) will be limited by controlling the reagent addition rate. Temperature of the reaction will be controlled by a combination of circulating cooling water through the reactor jacket and controlling the reagent addition rate. By limiting the hypochlorite addition rate, pH control and oxidation-reduction potential will be more easily monitored and controlled. If necessary, sodium hydroxide solution is added to maintain a sufficiently high pH. If complexed cyanides are not present, the waste is processed until the total cyanide (as CN⁻) is below 0.2 mg/L.

After the cyanide oxidation, additional hypochlorite is added if no excess exists, and the pH is lowered to 8.5 (reaction 2). After one hour, operators check for cyanate. When the concentration is below ~0.2 mg/L, the reaction is complete.

Excess hypochlorite is neutralized by adding dry sodium thiosulfate in stoichiometric amounts (reaction 3). Final pH adjustment to 6-7 pH is made by adding caustic (reaction 4).

Further chemical treatment is not necessary before the waste is discharged (assuming other waste types are not present). The treated waste solution from the treatment process is discharged through the recessed plate filter followed by polishing filtration as needed. Any solids recovered will be immobilized in a drum using cement, sand, and water (or other solidification system), allowed to solidify, and disposed in a landfill. The treated waste solution may be solidified in cement and landfilled or sent for further wastewater treatment. The fate of the liquid effluent depends on the waste classification and whether it is radioactive.

**Ammonia Destruction**

At basic pH, free ammonia gas exists in equilibrium with aqueous solutions containing the ammonium ion. Free ammonia, which evolves from these ammoniacal solutions, is destroyed by oxidation with calcium hypochlorite. For solutions containing cyanide, oxidation is concurrent with cyanide oxidation. Ammonium solutions that do not contain cyanide will undergo oxidative treatment for ammonia destruction. This process will free metals from their ammonium complexes, making them available for removal in subsequent processing. There is no EPA BDAT for ammonium solutions.

Ammonium metal complexes are in equilibrium with the ammonium ion. These complexes can interfere with the precipitation processes described below. Destruction of the ammonium ion results in an equilibrium shift away from the complex, eventually destroying all metal ammonium complexes.

The products of oxidation with calcium hypochlorite are nitrogen, calcium chloride, and water as shown in overall reaction (1) for pH above 8.5.

\[
\begin{align*}
4\text{NH}_3 + 3\text{Ca(OCl)}_2 & \rightarrow 2\text{N}_2\uparrow + 3\text{CaCl}_2 + 6\text{H}_2\text{O} \\
2\text{Ca(OCl)}_2 + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + 2\text{CaCl}_2 \\
\text{H}_2\text{SO}_4 + 2\text{NaOH} & \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \\
\text{Cl}_2 + 2\text{NaOH} & \rightarrow \text{NaClO} + \text{NaCl} + \text{H}_2\text{O}
\end{align*}
\]

- oxidize ammonia
- reduce excess hypochlorite
- neutralize sulfuric acid
- formation of sodium hypochlorite in scrubber

Excess hypochlorite is removed using the same method as for cyanide. Reduction of chromium and removal of heavy metal follow ammonia destruction if they are present in the waste.
Chromium Reduction and Removal

Hexavalent chromium (Cr\(^{VI}\)) must first be reduced to the trivalent form (Cr\(^{III}\)) before precipitation as trivalent chromium hydroxide. Sodium sulfite, sodium bisulfite, sodium metabisulfite, sulfur dioxide, sodium hydrosulfide, and ferrous iron are potential reducing agents. Because this technology requires the pH to be in the acidic range, cyanide or sulfide solutions must be pretreated to eliminate the possibility of toxic HCN or H\(_2\)S gas formation. The reduction and precipitation process for chromium is considered EPA BDAT.\(^4\)\(^5\)

For chromium-containing solutions that have been oxidized to remove cyanide or for plating wastes derived form chromic acid, all the chromium ions are in the Cr\(^{VI}\) oxidation state, the most environmentally unacceptable. The chromium is reduced to its Cr\(^{III}\) state before being precipitated for removal by filtration. The reduction step (reaction 1) is done by using sodium sulfite at a pH of 2-3 according to the following reactions.

\[
\begin{align*}
H_2Cr_2O_7 + 3Na_2SO_3 + 3H_2SO_4 &\rightarrow Cr_2(SO_4)_3 + 3Na_2SO_4 + 4H_2O &\text{reduce the Cr}^{VI} \text{ to Cr}^{III} \\
Cr_2(SO_4)_3 + 3Ca(OH)_2 &\rightarrow 2Cr(OH)_3F + 3CaSO_4F &\text{precipitate the Cr}^{III} \\
\end{align*}
\]

The chromium reduction process is operated in a batch mode. The amount of reducing agent is controlled by operator observation of oxidation-reduction potential and pH. When the correct oxidation-reduction potential and pH have been reached, the operator analyzes the reactor liquor for Cr\(^{VI}\) and then begins the precipitation step.

After the reduction step is completed, precipitation is done by adding caustic or calcium hydroxide until a pH of 8 is reached (reaction 2). The insoluble Cr\(^{III}\) hydroxide is filtered from the solution. Magnesium hydroxide may be added in varying degrees to aid in precipitate formation.

Following precipitation, filtration separates the solids from the waste water. Adding a filter aid or polymeric flocculating agents may be necessary to help filter any finely dispersed or gelatinous solids. A recessed plate filter is used for primary filtration followed by a cartridge-type polishing filter.

The solids are discharged from the plate filter into a 55-gallon disposal drum. Cement, sand, and water are added to the drum, the top closed, and the drum agitated using a tumbler-type drum mixer. After agitation, the drum contents are allowed to solidify before disposal.

The filtrate is either discharged to an acceptable recipient or recycled to the reactor for further treatment. The treated waste solution may be solidified in cement and landfilled or sent for further water treatment. The fate of liquid effluent depends on the waste classification and whether it is a low-level waste.

Precipitation and Separation of Heavy Metals Under Alkaline Conditions

Metals other than chromium contained in the plating waste solutions are precipitated, separated, and immobilized in a cement matrix. The process is based on the fact that most metals form insoluble hydroxides or sulfides. Because most metal sulfides are less soluble than metal hydroxides at alkaline pH levels, heavy metal can be removed more completely using sulfide rather than hydroxide as a chemical precipitant. Further, metal sulfides are much easier to separate by filtration or settling than are metal hydroxides. Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation for removing various heavy metals from plating wastewaters and is considered EPA BDAT. Soluble sulfide salts, such as sodium hydrosulfide, are used to precipitate many heavy metals. Metal sulfide precipitates normally pass EPA’s testing procedure for toxic metals.
Using acidic sulfide precipitation for metals stabilization has two disadvantages. First, the acidic conditions lead to the potential for hydrogen sulfide evolution, and second, treating wastes with both chromium and heavy metals complicates processing, as shown above. An alternative to acidic sulfide precipitation is to use sulfide precipitation at a pH greater than 10. Using this alternative, hydrogen sulfide evolution potential is substantially reduced, and all toxic metals can be immobilized. The alternative techniques will require piloting to select the most effective and safest method.

This technique begins by reacting calcium oxide in water to form calcium hydroxide slurry (reaction 1, below). Next, the acidic metal waste solution is added to the calcium slurry until the pH has dropped to around 10 (reaction 3). This step forms a metal hydroxide precipitate and a calcium nitrate byproduct. A 15% solution of sodium sulfide is then added to the slurry (reaction 4). The sulfide combines with metal ions in equilibrium with the metal hydroxide precipitate. Because the metal sulfide is less soluble than metal hydroxide, the consumption of metal ion from solution tends to cause the metal hydroxide to slowly dissolve. By keeping free sulfide ions present, all metal hydroxide precipitate is consumed, and the ultimate residual metal ion in solution will reach a level substantially less than that with the metal hydroxide.

\[
\begin{align*}
\text{CaO} + \text{H}_2\text{O} & \Rightarrow \text{Ca(OH)}_2 \\
\text{HNO}_3 + \text{Ca(OH)}_2 & \Rightarrow \text{Ca(NO}_3)_2 + 2\text{H}_2\text{O} \\
\text{M(NO}_3)_2 + \text{Ca(OH)}_2 & \Rightarrow \text{M(OH)}_2 + \text{Ca(NO}_3)_2 \\
\text{M(OH)}_2 + \text{Na}_2\text{S} & \Rightarrow \text{M}_2\text{S}_2 + 2\text{NaOH} \\
\text{HNO}_3 + \text{NaOH} & \Rightarrow \text{NaN}_3 + \text{H}_2\text{O}
\end{align*}
\]

make calcium hydroxide slurry \hspace{1cm} \text{(1)}
neutralize excess acid \hspace{1cm} \text{(2)}
precipitate metal as hydroxide \hspace{1cm} \text{(3)}
precipitate metal as sulfide \hspace{1cm} \text{(4)}
pH adjustment \hspace{1cm} \text{(5)}

The EPA upper corrosivity limit is pH 10 for discharge of a liquid waste. Because reaction (4) creates a caustic sodium hydroxide component, the solution pH will have risen from the starting 10 pH to above 12.5 pH. Reaction (5) is a simple pH adjustment using weak hydrochloric acid.

The scrubber system is a caustic scrubber that will capture any hydrogen sulfide evolved from the reactor. The scrubber solution must be maintained at a basic pH to prevent re-evolution of hydrogen sulfide gas. Peroxide is added to destroy soluble sulfide.

Following full precipitation and pH adjustment to below 10 using reaction (5), the waste is filtered through the recessed plate filter. Adding filter aid or polymeric flocculating agents may be necessary to help filter any finely dispersed or gelatinous solids. Following filtration, the solids are discharged from the plate filter into a 55-gallon disposal drum. Cement, sand, and water are added to the drum, the top closed, and the drum agitated using a tumbler-type drum mixer. After agitation, the drum contents are allowed to solidify before disposal.

Filtrate is further clarified using a polishing filter. The final filtrate is discharged to an acceptable recipient. The treated waste solution may be solidified in cement and landfilled or discharged for further water treatment. The fate of the liquid effluent depends on its waste classification and whether its radioactivity classifies it as a low-level waste.

**Acid or Base Neutralization**

This unit can be used for simple acid or base neutralization of nonplating waste solutions. The waste solution must be analyzed to ensure correct reagent selection. Very concentrated waste solutions may need dilution with water to help control temperature and to maintain enough volume for mixing within the reactor. After a neutral pH is reached, the waste solution is discharged to an appropriate container by pumping through the polishing filter. If neutralization creates appreciable solids (such as the neutralization of calcium hydroxide with sulfuric acid), filtration using the plate and frame filter may be necessary.
CONCLUSION
Los Alamos National Laboratory has designed and will be fabricating a movable treatment unit to treat mixed waste containing chemical and plating wastes. The unit will be used to treat waste at various DOE locations. Using best developed available technology and employing a simple but flexible flowsheet, the chemical plating waste treatment system can handle waste streams containing cyanide, ammonia, chrome, other heavy metals, and corrosive solutions.

REFERENCES