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Project Summary

Electroplating Plant Operating Conditions Related to Wastewater Sludge Leachability

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The objective of this project was to characterize the operating variables and wastewater sludges from six electroplating plants conducting a wide variety of plating operations so that the information developed would be applicable on an industry-wide basis. The results of the study in which untreated wastewaters were collected from each of six AES member plants, chemically treated to provide solid waste sludges are presented. The solids were separated, and the effluents analyzed for hazardous metals. All of the sludges were subjected to the ASTM "Method A" extraction procedure and hazardous metals analyses were conducted on the leachate. During the study, the EPA Extraction Procedure (EPA-EP) was distributed nationally. As the EPA-EP was one test of the hazardous properties of electroplating sludges under the Resource Conservation and Recovery Act (RCRA), the EPA-EP tests, rather than the ASTM Method A extraction procedure, were replicated for the six plants. All tests, chemical treatment, pH, separation, sludges generation, and extraction procedures were replicated. An in-depth statistical study was also performed of the analytical data for which sufficient information was available.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Background

An earlier study,* from which the current study developed, thoroughly investigated the wastewaters and attendant sludges from 12 electroplating shops. To utilize the data generated from the earlier study, six of the participating plating shops were selected for this current project. Selection was based on the variety of metals utilized, the wastewater treatment system, and the leaching characteristics of the plants' sludge. The presence of cadmium in the plants' wastewater was highly desirable as cadmium appears to be a problem with regard to its leaching characteristics. The facilities selected for this study showed significant quantities of cadmium, chromium, nickel, zinc, copper, and aluminum present in their wastewater and sludge. Two additional selection factors included: 1) good cooperation from plant management, and 2) the plants' sludge had U.S. Environmental Protection Agency - Extraction Procedures (EPA-EP) extract levels above the hazardous limits. This last factor was considered to demonstrate the benefits of the current project, if indeed, the sludges could be rendered nonhazardous by EPA's definition.

Approach

The purpose of the overall test program was to determine the effect of wastewater treatment chemicals and the pH on the leaching characteristics of

*Meredith, J. W., J. A. McCarthy, and A. Procko. Electroplating Wastewater Sludge Characterization. EPA-600/2-81-064, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1981.

sludges generated. The effect of the treatment chemicals on the dewaterability of the sludges by filtering and centrifuging was also to be determined. As a means to accomplish these goals, a detailed test plan was prepared that covered: (1) wastewater preparation; (2) simulation of the plant treatment; (3) screening tests; (4) dewatering tests; and (5) analysis. Screening tests were to be performed to determine the combination of precipitation chemical and pH which would produce a sludge with the best leaching characteristics without reducing effluent quality. Dewatering of the sludge produced by each treatment chemical followed, utilizing the pH value at which each chemical performed best during the screening tests.

Screening tests were conducted to determine the relationship between treatment chemical and pH on the treatment system effluent and on the extract from the sludges produced. The method utilized to achieve these goals was to take actual untreated electroplating wastewaters and treat them with three common neutralization chemicals: sodium hydroxide (NaOH), soda ash (Na_2CO_3) and lime (CaO). Tests were conducted with each of these chemicals on the untreated plant wastewater with pH's adjusted to 8.5 and 10 (7, 8.5, and 10 for Plant 7). The wastewater was treated in a manner similar to the plants' treatment system (except for the change in chemicals and pH) so that the plants could easily implement any recommended changes. Individual waste streams were mixed in the proper proportions, and kept agitated while pH was adjusted. Appropriate retention times were used, and after flocculation the mixture was allowed to settle. The water layer (overflow) was decanted and analyzed for its metal content and the sludge layer (underflow) was vacuum filtered. An analysis of the filtrate for metals was performed for comparison to the plant effluent. The sludge cake was then subjected to the American Society for Testing and Materials Method "A", extraction procedures (ASTM-A) and EPA-EP, the extract of which was also analyzed for metals (Figure 1).

To study the leaching characteristics of the screening test sludges, a portion of each sludge after filtering was washed in a filter funnel with 200 ml of deionized water and again vacuum filtered and the sludge subjected to the ASTM-A and EPA-EP. The washing water was also analyzed for metals.

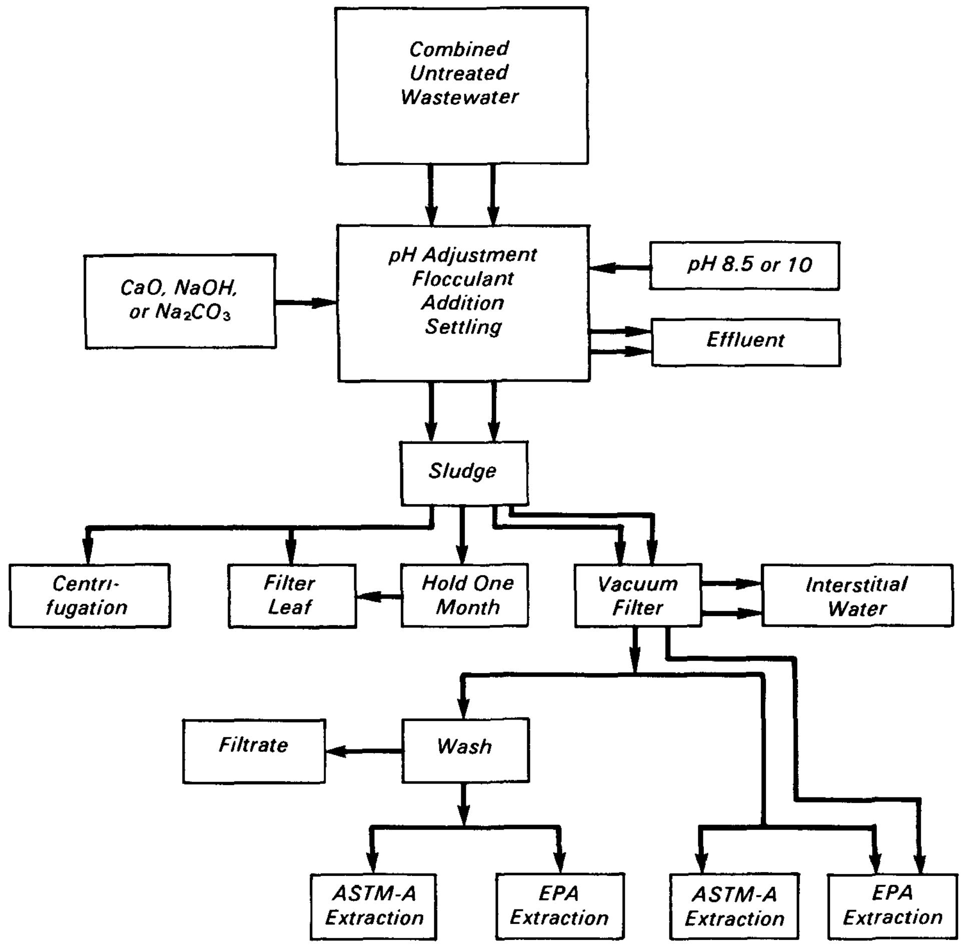

Figure 1. Test program and analytical plan.

Results

For Plant 2, at pH 10.0 more than 98 percent of the cadmium had been removed by treatment. Chromium and zinc were removed from the effluent with a 99^+ percent efficiency. At this pH, CaO showed the lowest metal levels in the effluent, although the difference is slight and although the metals did not resolubilize and leach out during the ASTM-A procedure, the lower pH of the EPA-EP caused Plant 2 to fail the EPA-EP based on cadmium levels. Results of the EPA-EP at pH 8.5 showed lower metal levels, but failed to pass the EPA-EP test. The chromium extract also failed the first time, but passed during the replication phase. Chromium levels in the effluent and EPA-EP extract were not affected very much by pH or chemical, except when Na_2CO_3 was used. With Na_2CO_3, chromium was an order of magnitude higher in the EPA-EP extract.

A similar analysis for Plant 3 shows cadmium and chromium removal efficiencies of 91 and 68 percent, respectively, at pH 8.5. At pH 10, cadmium and chromium removal efficiencies were 93 percent and 56 percent. At either pH, the plant's sludge failed the EPA-EP based on cadmium. However, cadmium performed very well during the ASTM-A procedure by not resolubilizing and leaching out, as chromium did. Chromium levels in the plant effluent were more affected by pH than by chemical, while cadmium was affected by both. Results of the EPA-EP testing showed 1000 times higher levels of cadmium to be present than did results of the ASTM-A. Chromium levels did not vary with the two tests and appeared to be independent of chemical, and only slightly dependent on pH.

For Plant 4, at pH 10 chromium was removed from the effluent with an 81-percent efficiency, copper was removed with 84-percent efficiency, and nickel was reduced by 85 percent. Although CaO did not show a clear superiority with the effluent samples, it was most clearly the best overall performer for the EPA-EP and ASTM-A testing. Plant 4 was one of two plants that would have passed the EPA-EP based on these screening tests At a treatment pH of 10, metal levels in the plant effluent and EPA-EP extracts were always lower when using CaO. Although the metals did not resolubilize and leach out during the ASTM-A procedure, the lower pH of the EPA-EP caused considerably higher metals levels in the extract. Metal levels were higher by two orders of magnitude in some cases.

For Plant 6, at pH 8.5 chromium was reduced by 99 percent and nickel by 97 percent in the plant effluent. Chrome in the untreated wastewater was 2½ times higher than nickel, although this difference was not evident in the plant effluent. Results of the ASTM-A on the plant sludges showed no significant leaching for either chromium or nickel. During the EPA-EP greater quantities of metals were seen to leach in some cases by as much as 100-fold. The plant's sludge did not consistently pass the EPA-EP. During the first series of tests, all sludge samples passed. However, at pH 8.5 two samples failed during the replication, based on chromium. Best results for the EPA-EP were obtained with treatment at pH 10.

For Plant 7, at pH 8.5 more than 97 percent of the cadmium had been removed by treatment. It is also evident that the cadmium had not resolubilized and leached out of the sludge during the ASTM-A procedure. Copper was removed from the effluent at approximately a 95-percent efficiency. With the exception of the lime test at pH 10, the copper found in the ASTM-A extract did not resolubilize to a large extent. The exception noted leached at a concentration three to four times higher than the copper concentration in the untreated water. Chromium, nickel, and zinc were present in much higher quantities in the untreated wastewater than were cadmium and copper. Chromium was removed from the water at approximately a 98-percent efficiency regardless of chemical or pH. The quantity leached, as measured by the ASTM-A extraction procedure, tended to decrease as the pH of the treatment increased. The removal of nickel from the wastewater is very obviously dependent on pH and only slightly dependent on treatment chemical with NaOH performing somewhat more effectively than CaO or Na_2CO_3 as pH increased. Removal rates were approximately 90 percent at pH 8.5. Nickel levels in the sludge leachate were affected by both pH and treatment chemical. At a treatment pH of 10 both the CaO and NaOH generated sludges leached very high levels of nickel while the Na_2CO_3 sludge leached less by a factor of 10. Zinc removal from the wastewater approached 98 percent with little difference between chemicals and with minimal pH effects. Sludge leaching test results varied with respect to treatment chemicals.

During the screening tests for Plant 7, the EPA-EP was not performed. Instead, a series of leaching tests were performed on larger batch samples prepared at the pH value which gave best results with each treatment chemical during the screening tests. In the leaching tests, as with the screening tests for this plant, none of the metals seemed to resolubilize and leach out of the sludge during the ASTM-A procedure. Metal levels in the EPA-EP were generally higher than the ASTM results.

In order to derive a measure of the statistical significance of these Plant 7 large batch test results, the ASTM procedure was applied to washed sludge precipitated by each of the three chemicals a total of three times. This replication provided the ability to calculate the experimental variation due to chance alone. The test for statistical significance is based on the ratio of the variation in leachate concentration (for each metal) from one treatment chemical to another to the variation due to chance (the F-statistic). Any observed dependence on treatment chemical is significant if this ratio is large enough.

A one-way analysis of variance was performed based on the results. There were significant results at the 99-percent level. The dependence of nickel concentration in the leachate on the treatment chemical was signficant at the 95-percent level.

Results for Plant 8 at pH 8.5 indicate that chromium was removed by 96 percent, copper by 97 percent, and nickel by 96 percent from the untreated wastewater. The plant effluent results were best when using CaO. The use of Na_2CO_3 always gave higher metal concentrations in the effluent by at least tenfold over the CaO results. The ASTM-A procedure did not cause the metals to resolubilize and leach out as did the EPA-EP. The sludge from this plant failed the EPA-EP on the basis of chromium. Although the sludge would still have failed the EPA-EP, less chromium leaching occurred when treatment was with Na_2CO_3. If nickel were to be considered a hazardous material under RCRA, the use of Na_2CO_3 for treatment would need to be more thoroughly investigated as it works better for some metals than for others.

It should be remembered that direct comparisons between the EPA and the ASTM-A extraction procedures are not possible due to the differences in the amount of dilution water used in the respective tests. In the tests done during this part of the study, the EPA-EP extracts had a much higher water-to-solids ratio than the ASTM-A tests.

The analytical results of plant effluent and sludge filtrate show that the sludge's interstitial water (filtrate) had metal levels lower than the effluent. The kinetics of the precipitation reaction, are initially rapid, but very slow to reach equilibrium -- the point at which precipitation essentially stops. The interstitial waters are in direct contact with the sludge particles for a longer time than the effluent waters and therefore have more opportunities to take advantage of nucleation sites for precipitation. The net result is a lower level of metals in the interstitial water. This theory is reinforced by the observation that the filtrate from the washed sludges had metal levels lower than the filtrate from unwashed sludge. It is assumed that equilibrium had not yet been reached.

An unexpected observation was that for most cases cadmium and zinc levels in the EPA-EP extract were higher with the washed sludges than with the unwashed sludges. Chromium and nickel levels were generally lower in the EPA-EP extract of the washed sludge than in the unwashed sludges. It has been assumed that washing with deionized water would flush out the high metal levels expected to be found in the interstitial water. Similar mixed results were obtained for washed and unwashed sludges during the ASTM-A extraction where pH was not maintained. This seemed to indicate that this phenomenon was not pH related. It was apparent that washing sludges had no benefit from a leachability standpoint, and may actually have caused higher leaching if the sludge contained cadmium.

Certain observations appeared for one plant but could not be broadly applied to others in this study. An example of this comes from Plant 7. In every case except the unwashed cadmium sample, the sludges generated by Na_2CO_3 had higher metal levels in the EPA-EP extract than did those produced by CaO or NaOH. This effect was especially notable for chromium and zinc. These and other observations, as mentioned above, could not be applied to other plants in the study.

The effect of treatment chemical on the solids content of the sludges showed that calcium oxide, in general, resulted in treated wastewater streams with a higher total solids (TS) content while NaOH resulted in the lowest TS. For CaO and Na_2CO_3, the TS also tended to increase directly with pH, while TS was basically unaffected by pH for NaOH. Three treatment pH's were studied for Plant 7. With CaO and NaOH the suspended solids (SS) reached a maximum at pH 8.5 and then dropped off as the pH was increased to 10. SS increased with pH for Na_2CO_3.

Conclusions

The conclusions drawn as a result of tests conducted and observations made are valid only to the plants that were sampled; however, it is likely that the results will be generically useful to many electroplating shops with similar wastewater characteristics.

Considerable lack of agreement was found between the analytical results for replicate samples prepared by the same technique. This scattering effect gives a surprisingly high background or random variation. This is especially true in samples containing chromium (+6). Against such a background, only rather large changes in sludge leachability could be said to correlate to given treatment parameters with statistical significance. In spite of this masking effect, some correlations appeared to be significant, and the following conclusions can be drawn from the results:

- In the screening tests, the ability of wastewater treatment variables to influence extract quality by variation of treatment parameters was apparently plant specific. The ability to influence extract quality appears to vary among metals under consideration.

- Optimum flocculant and flocculant concentration were determined for each plant's wastewater. A simple jar test was developed to enable plant operators to do their own evaluations.

- The treatment chemical and pH affected the solids content of the wastewater sludges. The higher solids sludge was produced by CaO at pH 10. Less solids were produced by NaOH and Na_2CO_3 and were the same at pH 8.5 and 10.

- The leachability of metals was lower when performed by the ASTM-A extraction procedure than by the EPA-EP. The pH that produced the least leaching was different for each plant. The parameters (pH, treatment chemical, or interaction) that showed a statistical significance for a plant can only be said to be significant for that particular plant. No generalities could be found to apply to sludge leachability.

- The interstitial of free water associated with the sludges had lower metal levels than the effluent waters.

- The precipitation chemical had little effect on sludge dewatering by centrifuge and vacuum filtration. The fresh sludges that dewatered fastest during vacuum filtration all were at pH 8.5. In most cases, fresh sludge dewatered faster than aged sludge though not exclusively. Each plant's sludge behaved differently.

- No quick acceptance test related to the EPA-EP was found that could be broadly applied to all plants. Each individual plant may be able to develop a quick acceptance test that applies to its own sludge. However, potential for development of a quick-acceptance test for segregated landfills (ASTM-A) was discovered.

During the sampling portion of the study, it was observed that many waste treatment areas within the electroplating shops were not being operated as well as the equipment would allow. Control instrumentation in some shops was not being properly maintained and therefore could not treat the wastewater properly. In other shops, important indicators were missing so that the effectiveness of treatment was never known.

Recommendations

The following recommendations are based on observations made during the testing and engineering evaluations of the data.

- Additional data should be obtained and necessary analysis performed in order to derive a quick acceptance test for operators of segregated nonhazardous waste landfills, based on the significant correlations between filtrate and ASTM-A extract results found in the present study.

- The testing procedures and their evaluations should be incorporated into a "Standard Electroplaters Wastewater Evaluation Procedures," which can be of general interest and value to individual plant operators who wish to make their own in-plant studies.

- To determine the validity and magnitude of some of the more positive conclusions, such as the use of CaO or NaOH, selection of pH, the use of selected flocculants, etc., it is recommended that these variables be studied at one electroplating plant. The study would involve operating the plant under existing conditions, and then operating for a week at steady state with one or more selected changes. The testing of plant effluents and wastwater sludges would be analyzed and the data evaluated in the same manner as described in this report.

- The data for each plant participating in the study was given to plant management with a request for comments, suggestions and criticism. No replies were received. Perhaps the American Electroplaters' Society might be of assistance in obtaining feedback, even if it is of general nature.

- A study to determine the "in-practice" variability of the EPA-EP and the ASTM-A should be undertaken. This request has come from many others using the two procedures, and the data from this report also indicates the need for such a study.

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***Thomas J. Powers** is the EPA Project Officer (see below).*
The complete report, entitled "Electroplating Plant Operating Conditions Related to Wastewater Sludge Leachability," (Order No. PB 84-120 781; Cost: $19.00, subject to change) will be available only from:
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