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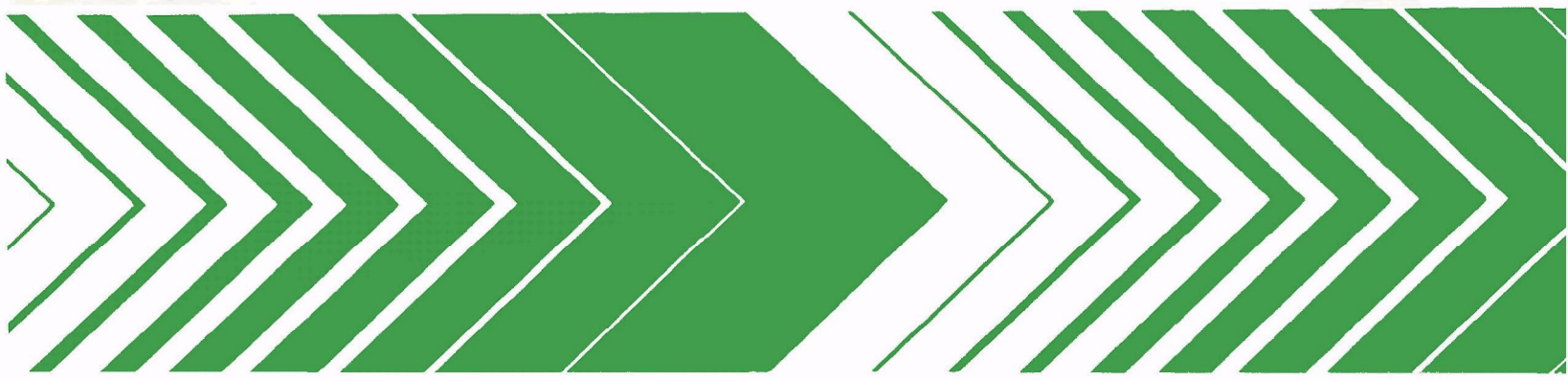
Second Conference on Advanced Pollution Control for the Metal Finishing Industry

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
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This report has been assigned to the "SPECIAL" REPORTS series This series is reserved for reports targeted to meet the technical information needs of specific user groups. The series includes problem-oriented reports, research application reports, and executive summary documents. Examples include state-of-the-art analyses, technology assessments, design manuals, user manuals and reports on the results of major research and development efforts.

Second Conference
On Advanced Pollution Control
For the Metal Finishing Industry

PRESENTED AT:
ORLANDO HYATT HOUSE, KISSIMMEE, FL
FEBRUARY 5 - 7, 1979

Co-sponsored by:
- The American Electroplaters' Society
- The United States Environmental Protection Agency

Disclaimer

Foreword

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

These proceedings cover the research papers and discussions of the "Second EPA AES Conference on Advanced Pollution Control for the Metal Finishing Industry." The purpose of the conference was to inform industry on the range and scope of research efforts underway at IERL-Ci to solve the pressing pollution problems of the metal finishing industry. It is hoped that the content of the conference and the subsequent proceedings will stimulate industry action to reduce pollution by showing through government-sponsored research at IERL-Ci that viable control options are available. Further information on these projects and other metal finishing pollution research can be obtained from the Metals and Inorganic Chemicals Branch, IERL-Ci.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

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INTRODUCTION

The U. S. Environmental Protection Agency's Metals and Inorganic Chemicals Branch and the American Electroplaters' Society, Inc., jointly designed a broad-scoped colloquium, "The Second EPA/AES Conference on Advanced Pollution Control for the Metal Finishing Industry," in Kissimmee, Florida, on February 5   7, 1979. The primary purpose of this conference was to perpetuate the dialogue established at the first EPA/AES meeting (1978) between key members of EPA and the metal finishing industry. The proceedings, contained herein, of this second conference reflect the focal points of the gathering: the status of EPA's wastewater and solid-waste regulations, and both EPA's and industry's research efforts to effectively deal with the ramifications of these regulations. Research on analytical methods and air-pollution control strategies was also addressed at the conference and reports of this work appear in these proceedings.

The program of the conference was broken into three segments: regulatory; research, design and development; and an exchange of viewpoints between members of government and industry. Since attendees of the first conference placed extreme emphasis on the problems of dealing with wastewater and solid waste, the primary purpose of the first segment of the second conference was to provide conference participants with a detailed understanding of the potential impact of current and future regulations in these two important environmental areas. Key EPA officials, representing the Effluent Guidelines Division (water) and the Office of Solid Waste, described the procedure by which EPA prepares and promulgates regulations, with special emphasis on direct impact to metal finishers.

The second segment was divided into five areas: (1) an overview of EPA's research program for pollution problems regarding air, water and solid waste as it relates to the metal finishing industry, (2) control of solid waste, (3) pretreatment of wastewater. (4) recovery of chemicals from wastewater, and (5) air-pollution control and methods of analyzing potentially harmful liquid and solid discharges. Programs sponsored by both EPA and industry were presented to provide the audience with a better understanding of the significant research and development in these five areas.
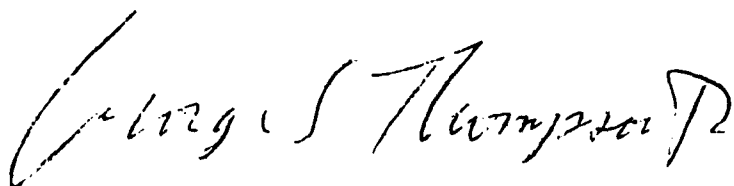
The third segment, entitled "Exchanging Viewpoints," was conducted during a three-hour evening session. A panel comprised of EPA officials and industry representatives opened the floor to a free discussion in order to permit EPA to clearly understand those research needs considered by the industry to be of paramount importance. This objective was fulfilled as research needs became evident during frank discussion between the audience and the panelists.
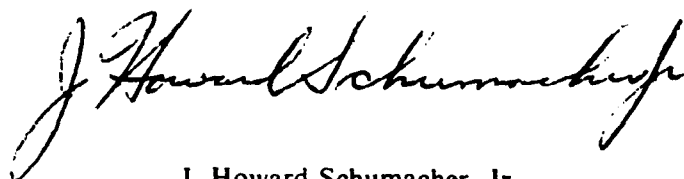
This conference, attended by more than 600 persons interested in the environmental problems faced by metal finishers, was considered an extraordinary success. The principal purpose of the conference, to continue a fruitful dialogue between industry and EPA, was achieved. The high-priority research needs of the industry were identified and solutions to pressing problems are being sought—some jointly—by EPA and AES.

The proceedings are published here in order that the important material presented at the Conference can benefit as many people as possible interested in solving the intricate problems inherent in metal finishing processes. These proceedings contain the presentations made by representatives of two EPA regulatory groups affecting the metal finishing industry, as well as presentations by various parties actively addressing research and development in this same environmental area.

The EPA and the AES are pleased to have cooperated in this mutual endeavor which has improved communications and which should foster continued research resulting in sound technical solutions to the environmental problems of metal finishers.

George S. Thompson, Jr.
Chief
Metals & Inorganic Chemicals Branch, EPA

J. Howard Schumacher, Jr.
Executive Director
American Electroplaters' Society, Inc.

EPA Welcome to the Second Conference On Advanced Pollution Control For the Metal Finishing Industry

Dr. Eugene E. Berkau*

I would like to extend to you EPA's "welcome" to this Second Conference on Advanced Pollution Control for the Metal Finishing Industry. In addition, I offer a special thanks to Howard Schumacher and his staff, to Jerry Schmidt, Dick Crain, Clarence Roy, and to other AES officials who have worked diligently to make the conference possible. We hope our efforts are successful in providing you with an understanding and an awareness of EPA's regulatory and R&D activities impacting the metal finishing industry.

We in EPA view this conference as a timely and cost-effective tool for us to obtain the metal finishing industry's evaluations of and recommendations for our ongoing and planned programs. Consequently, this conference is a critical activity in EPA's metal finishing R&D program. I think, for instance, that when you hear George Thompson's presentation on our metal finishing R&D program, you will see that much of the R&D work which has been initiated this past year resulted from your comments at the last year's conference. This year we again solicit your participation and comments after each presentation and particularly at the Tuesday evening discussion session to be moderated by Ken Coulter. Members of my staff who are responsible for the development and implementation of the metal finishing R&D program are George Thompson, Chuck Darvin, Fred Craig, and Mary Stinson. George and his people will be actively soliciting your comments and reactions during this conference's discussion periods and through informal contacts. We intend to compile this information and distribute it to you for comments along with the conference proceedings.

The major goals of the R&D efforts are to develop and evaluate pollution control methods that are broadly applicable to the metal finishing industry, that present cost-effective options for meeting regulations, and that minimize or eliminate intermedia transfer of the pollution problem.

At last year's conference we attempted to bring to you the status of EPA's total efforts in air, water, solid waste, and toxic substances which are likely to impact your industry. This year we are focusing on the Agency's water and solid waste programs which we feel will have the greatest impact in the near term.

I personally would like to encourage you to critically evaluate the ongoing and planned R&D activities in view of the R&D goals I have stated, and to provide your candid comments on each project and the overall program direction. Your participation is essential to the success of the conference and to EPA and the industry's efforts to control pollution from the metal finishing industry.

Once again, I am glad you are here and hope that I have the oppotunity to meet many of you during the next three days.

*Dr. Eugene E. Berkau, Director
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Status of Effluent Guidelines
And Pretreatment Activities of EGD

Robert B. Schaffer*

The final pretreatment regulations have not yet been made public. I will be able to tell you something today that will be of interest and importance to you. I do have one very serious constraint, however; it is the formal constraint not to discuss major issues with regard to proposed regulations between the close of the comment period and the final promulgation. So I apologize that I will not be able to discuss them in great detail today. However, there are a number of things that I can relate to you. I will relate a summary of the public comments that were received on the proposed regulations that are now in consideration. I may not touch on every one or one that you particularly submitted yourself, but I will try to give eight or ten general comments where we have received a number of comments. I hope to provide you with a feel of when we expect to make a final decision on those regulations. Following that, what I really can talk about and what I am primarily engaged in at this point of time, is our effort on the BAT Review which I am sure will be of interest to you. I can talk in detail about the effort— where we are, what our approach is, what we have found to date, and what we might do about it. So, with those preliminary notes, let me start by summarizing the comments that were received. There are other speakers from the Agency who will be discussing items of interest to you that relate to the guidelines and that is appropriate. I saw that Gary McKee will be here to talk on cyanide analysis. A representative from EPA's Office of Water Enforcement, who is intimately involved in the pretreatment regulations, will be here tomorrow night to answer questions with regard to how those regulations might be implemented.

Let's dive into the public comments. Number one on the list, believe it or not, is cyanide. Several comments received suggested that the analysis was not appropriate nor were the levels that were specified.

A number of commenters also suggested that cyanide was a compatible pollutant, that is, when discharged into a sewer it does not impact or pass through a treatment plant. In regard to cyanide, others are suggesting levels that might be more appropriate for pretreatment. They fall around 1 mg/liter of total cyanide.

Several commenters question the need for amenable cyanide limitations for wastes that are discharged into a publicly-owned treatment works. In this case, amenable cyanide was suggested as the only appropriate limitation, so we are getting comments on both sides of the issue.

Many folks expressed a concern with regard to concentration-based limitations and that they would penalize those facilities that were employing water conservation practices. An optional mass-based limitation was included in the proposal to overcome that problem.

There were many comments that addressed the total metals limitation that was suggested as one of the options. Many thought that it was not supported by the documents that were provided and that it would be very difficult to meet by certain facilities.

As you can imagine, we got many comments with regard to the impact of the regulations, some forecasting a higher impact than we thought, others forecasting a lower one. Generally, however, most thought they were understated and, therefore, our judgments in the proposal were not, in fact, economically achieveable.

In addition, there was a request by several commenters to include specific monitoring requirements in the regulations. Some commenters requested clarification as to whether or not daily sampling was required to meet a 30-day average and definition as to how the samples should be taken and composited over a working day. So, there was a bit of concern regarding monitoring requirements.

Many folks also felt that the cost for sludge disposal, which we placed at !2¢/gallon, is low. We did get additional estimates and additional data on costs that ranged from 25¢ to $1 per gallon. Also, there were many comments that requested that EPA participate actively in establishing a national network of disposal sites. Maybe Jack Lehman will be talking to you about that very topic and be able to answer questions about that.

There was an additional comment as to whether or not hexavalent chromium was an appropriate limitation, since the waste discharges into a highly reducing environment (the sewers) and that the hexavalent chromium will be rapidly reduced to the trivalent state. Therefore, the limitation was not necessary. A limitation on total chromium was suggested as the alternative.

There were many comments concerned with the small plater cutoff. Concern about small platers disrupting

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small sewage plants was voiced and it was suggested that the regulations were not nearly stringent enough. There was a particular request that the Agency specify the state and local government's right to impose stricter regulations.

We have had two sets of regs, one for interim final which cover cyanide destruction and hexavalent chrome reduction. The compliance data is July 12, 1980. We expect we will go "final" with the second, the proposed pretreatment regulations sometime in the middle of this calendar year. That will initiate the time clock for achieving these limitations as three years after that date. As you may be aware, this was done purposely in order to stretch out the time that would be required for compliance with both regulations in order to minimize the overall economic impact.

That covers the major comments that we have received to date—they are public information, they are available in our offices and will be made available through information services once they are all catalogued and compiled.

I would like to turn now to our ongoing work with regard to our BAT studies. As you know, we will be reviewing all of the previous regulations, interim final and proposed, with regard to the toxic pollutants that were included in the 1977 amendments that I am sure you are all familiar with. We have, as far as our approach goes, expanded the list of chemicals that were identified in the amendments from 65 to 129. We are proceeding to evaluate various discharges, in all industries, electroplating being one. Our initial effort evaluates each subcategory and screens the discharge. Screening means taking a representative sample from a number of plants in a subcategory and running a very sophisticated chemical analysis on it. These analyses (GCMS, Gas Chromatography Mass Spectrometry) are expensive. It is pushing the state-of-the-art as far as analytical capabilities are concerned and is one reason why the Agency undertook to do the sampling and analysis itself. This particular analysis looks at 114 of the 129 pollutants that are of concern to us. In this first effort our primary objective is to identify the presence or absence of these 114 organics and to roughly quantify the amount that is present. We do this in order to be able to focus our attention on the organic pollutants of primary concern so that when we go back and take a further look we will be able to focus in on things that are of most significance. We will then run through what we call a verification program, wherein we once again confirm the presence or absence of the materials that we found and make an effort to quantify them and to evaluate the appropriate technology for their removal. The costs are also determined. We will then take this information and go through much of the same procedures that were gone through in previous guideline efforts.

Since we do not have "approved" methods for many of these materials, and in the Clean Water Act there is a section which requires analytical methods to be approved before they can be used in Permits, we have had to look at

various other options of regulating. We are looking at indicators. We are looking at surrogates. We are looking at the need for specifying the limit for each of the 114 pollutants that we have found. One of the things we are considering in this is the treatability or compatibility of these organic materials with POTWs. We have a pretty substantial effort underway to try to determine whether or not these materials will be adequately treated in a municipal system, whether or not they pass through, whether they have an adverse impact on the disposal of the sludge. We will be taking all of these into consideration as well as the volume and mass of materials that are being discharged to determine whether or not the regulation is appropriate. It is conceivable that the study we have underway will be equal in stringency to our previous regulations or more stringent than those regulations, depending upon the levels of these priority pollutants, the treatability of these pollutants, and the discrimination as to necessity of regulation. We, of course, found a few metals in discharges, as we expected, but we also did find some organic materials present. There were probably fifteen to twenty depending on the particular subcategory and we have made a determination as to which ones we are going back to look at in more detail. For your information, those which we have found to be most prevalent are 1-1 trichlorethane, 1-2 trichlorethylene, methylene chloride, bis$_1$-hexylphthalate, and toluene. The levels that we have found range between five micrograms per liter and 200 micrograms per liter. The rough total of toxic organic pollutant levels that we have found to date is about 300 micrograms or 0.3 mg per liter. We had a suspicion that we would find some of these because some of them are found in some degreasers, etc. that we might have in job shops. Phthalates, which we are finding everywhere, come from plastics. Anytime that water comes in contact with plastic, we seem to find certain levels of these phthalates. There is an environmental concern with regard to all these pollutants. We will be publishing, for instance, the frequency of the presence of these materials in waste waters. To achieve proper control of the serious problems that we find, we will be again promulgating four sets of regulations from this study. We expect to review BAT, Best Available Technology Economically Achievable, for direct dischargers. We expect to be reviewing in detail and ultimately modifying pretreatment regulations and we will be establishing new source performance standards for both direct and indirect dischargers. We are looking closely at new source performance standards. We feel that in an industry, where there is rapid growth, or where there is significant impact, that one of the most important long-range things that we can do is to establish very tight, new source performance standards. The design options, location options, and a number of other options make it much easier to take steps to control toxic pollutants when a particular facility is constructed. We also expect that any revised standards that come out separately will be built upon, and compatible with, the other regulations that either have been promulgated or proposed.

I do not believe that we are going to invent a new technology with these regulations. We hope there are new technologies available at your option, but they will be built upon, and we expect, compatible with those that we have been discussing over the years. We do not have a present schedule for our BAT studies and we expect them to be proposed March 21, 1980. We will then expect the promulgation to occur in October of 1980 which would provide a three-year compliance time, in the area of pretreatment, as has been the period for the interim final and proposed pretreatment regulations.

We appreciate your continued interest and participation with us and expect, once we are over the hump on our promulgation of the pretreatment regulations, to be back into more detailed discussions, etc., with respect to our BAT study. We continue to invite your participation, with your technical committee and with you individually, if you so desire.

Status of Office of Solid Waste Activities

John P. Lehman*

My purpose in talking to you today is to discuss the hazardous waste regulations that have been sanctioned by RCRA.

The proposed RCRA regulations, which are out for public comment now, emphasize the responsibilities of the generators of waste. It is the generator's responsibility to make the decision as to whether or not he has a regulated waste as defined in Section 3001. There are a number of other requirements for generators in the Section 3002 regulations. Although some generators do dispose of the wastes in what we call on-site facilities, these regulations apply to both on-site as well as off-site disposal cases. This non-distinction regarding disposal location is very important. Most state programs deal only with off-site facilities. The federal program and all future state programs will deal with both on-site and off-site disposal of solid waste.

Let's assume that a waste will be shipped out for off-site disposal. It is the generator's responsibility to prepare a transportation manifest which accompanies the wastes. First, the generator must determine, in advance, that the facility to which he is sending the waste has a permit to accept the type of waste that is being sent. The generator fills out a manifest and gives it to the transporter. The transporter is required by the Section 3003 regulations, proposed in April of 1978, to take the wastes only to the facility which has been designated by the generator. If any spills occur en route, the transporter is required to report it back to an emergency number. He is subsequently required to clean it up.

The disposer is subject to the disposal regulations, called facility standards, in Section 3004. In effect, these define what constitutes the environmentally acceptable management of hazardous wastes. These standards cover treatment, storage, and various types of disposal, including incineration, treatment, surface impoundments, landfills, landfarms, basins. You name it—it is there in these regulations.

The permit regulations under Section 3005 codify the technical requirements in Section 3004. The permit regulations are, in fact, mainly administrative regulations. They state what you have to do to apply for the permit; where you send it; the permit application's contents; what happens once the permit application gets into the system; the due process; the public hearings. The

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Administrator of the Agency is in the process of consolidating this type of administrative ruling for three different programs—the RCRA Hazardous Waste Program, the NPDES Discharge Program under the Clean Water Act, and the Underground Injection Control Permit Program under the Safe Drinking Water Act. These are still in process, but the consolidated permit regulations are scheduled for proposal sometime later this month. So that is basically the flow of it.

Several other aspects to this program are really important. Section 3006 deals with state programs. It was very definitely congressional intent, in RCRA, that the Federal government write the national standards, but that states carry out the programs in lieu of the Federal government. This is very important wording in RCRA. Similar wording is not in the Federal Water Pollution Control Act; nor in the Safe Drinking Water Act. There, the states may be authorized to carry out this program instead of the Federal government. In RCRA, the states are not merely delegated a Federal program—they have their own program which may or may not be identical to the national one. However, if it is equivalent to and consistent with the federal program, other state programs, and has adequate enforcement, the Administrator of EPA is required by the law to authorize the state's program to operate in lieu of a Federal program. Therefore, the Section 3006 regulations are an exposition of what we believe equivalency, consistency and adequate enforcement mean with respect to state programs. These were proposed one year ago in February 1978.

We were going to finalize these regulations when the current efforts to consolidate the regulations (Resource Conservation and Recovery Act, Federal Water Pollution Control Act, and Safe Drinking Water Act) were initiated by the Environmental Protection Agency last summer. The Agency is currently consolidating the state program requirements for the RCRA Hazardous Waste Program with the NPDES (FWPCA) and the Underground Injection Control Regulations (SDWA) so that there will be one set of regulations that apply to state program authorizations. Where these statutes differ, there will be different sections in the regulations. There will be a general section which applies to all three Acts (Section A) and then Sections B, C, and D to deal with specifics of each individual program. Here it is tied with the Consolidated Permit regulations and will be reproposed, since these changes were made to it, on the same schedule as the Permit regulation.

Most of the regulations that I have talked about to date are in Part 250 of the Code of Federal Regulations. The consolidated permits and consolidated state program regulations will be issued under Parts 122, 123, and 124 of the Code of Federal Regulations.

Last, but not least, is Sectin 3010, a notification or registration requirement that is in RCRA. What the Law says is that, once the Agency defines a hazardous waste under Section 3001, everyone who is included in this new system, that is anyone who generates, stores, treats, transports, or disposes of any waste which is identified as hazardous under Section 3001, must notify EPA within 90 days. This Section is, in effect, saying what kind of notification information is required and suggests a sample data format to be used. The Agency will use a massive computer mailout to make it easy for everybody to understand the regulations with which they are supposed to comply. This regulation was proposed in July of last year. The comment period has closed and OSW is preparing the final regulation. Therefore, as with Bob Schaffer's pending effluent guidelines and regulations, I will not be able to answer too many explicit questions about Section 3010.

Section 3001 is an important regulation. It describes two different ways to define hazardous wastes, both prescribed by the Act. Hazardous waste is defined by both general characteristics and by lists. Under general characteristics, four have been proposed. The first is ignitable waste, chosen to avoid confusion with the term used for flammable materials by the Department of Transportation. Both use the same type of test technique: a basic flash test to test the ignitibility of wastes. Corrosive wastes are characterized based on pH for strong acids or bases. Reactive wastes include most explosives and anything that is of a pyrophoric nature. And lastly, we have a characteristic for toxicity which is related to the groundwater and, therefore, tied to the primary drinking water standards. These standards, at the present time, deal only with heavy metals and some pesticides, and do not include a great number of organic chemicals.

The first of the lists is the list of generic wastes, such as solvents, cutting oils, etc., that are found in almost every industrial category. Second, we found that the best way to deal with infectious wastes was to list the sources of infectious wastes. Certain kinds of laboratories and departments in hospitals constitute this second list. Next, and this is really the heart of it all, process wastes have been listed by SIC code. The intent was to make the regulations easy on the generator. Rather than saying, for example, wastes that contain mercury in concentrations greater than 5 parts per million are hazardous, which would imply that everybody had to run out and test their wastes for mercury to see whether they had more or less than that amount, that decision has been made for you. Wastes from certain types of processes that EPA expects have a high content of hazardous materials are covered. We have listed wastes by process; therefore, no testing is required. If an industry waste is on a list, it is in the

control system. There are about 175 wastes in those first three lists.

In addition, we are faced with the problem of people throwing away pure chemicals. Consider a bad batch in a production process that is off spec or chemicals for which the shelf life is over. These wastes fall into a fourth type of list in which we reference the DOT poison A and B categories, the priority pollutants, and the rebuttal presumption pesticides. In other words, discarded pure or almost pure chemicals that are on those lists are also in the system. There are about 275 of those waste chemicals listed. So, overall, there are on the order of 450 items that are on the hazardous waste lists.

Now, each of the four characteristics I mentioned earlier is keyed to a test protocol to determine whether or not a waste meets those characteristics. Probably the most interesting and perhaps the most controversial aspect of the regulations is related to the toxicity characteristic. The test procedure is called the extraction procedure (EP). What the extraction procedure is supposed to do is to provide a model of what might happen to a waste if it is improperly disposed. In other words, can toxic constituents of the waste leach under reasonably normal conditions of rainfall, etc.? Will that material leach out of the waste in sufficient quantities to present a threat to groundwater and hence to drinking water? It is basically a screening mechanism to help decide what is and is not a hazardous waste. As I mentioned, there is not a general characteristic for organics but we have in the December 18, 1978 Federal Regulation, an Advanced Notice of Proposed Rulemaking indicating the Agency's intent to develop a method for organic toxicity related genetic change potential, for phyto-toxicity and several other forms of toxicity. The comment period on the Advanced Notice of Proposed Rulemaking closes on July 1, 1979, so if there are comments on the proposal, you will have until July to comment on that.

There is also a "delisting" protocol. The Agency recognizes that, particularly in the process stream categorization, there may be a certain waste stream within an industry SIC code that is not hazardous even though a generalization about that particular industry would indicate that it is. Individual facilities may show EPA that a waste, even though it is listed, is, in fact, not hazardous. Following the protocol, it can be taken off these lists or "delisted."

Generators are responsible for many things under these regulations. First of all, I mentioned they are responsible for making the basic decision, "when is a waste a hazardous waste?" This can be done in three ways. First, they check the various lists and see if their waste is on any of the lists - the only decision we make for them. Second, they can test their waste against those characteristics that are defined or, last, they can just simply declare the waste to be hazardous and enter it into the system. Generators are also required to prepare the shipping manifest mentioned previously, to keep records and to make reports.

There are certain exemptions, however. First, all household wastes are exempted because that was cited in the legislative history. POTW sludge is exempted because the Clean Water Act Amendments of 1977 called for regulation of municipal sludge under Section 405 of that Act. Industrial sludge is not exempted. A conditional exemption is provided to retail establishments and farmers provided that they dispose of their wastes in state approved facilities. There is one last exclusion which is very controversial. If you would like to comment on this, we would be happy to have you do so. There are a very large number of potential sources of hazardous wastes, but a great majority of those generate waste in a relatively small quantity. In other words, there is a very sharp break in solid waste generation quantities, as most of the wastes are generated by a relatively small number of large generators; and yet there are a large number of generators producing small amounts. So, what we have tried to do here is balance the risk to the environment of having relatively uncontrolled amounts of waste against all of the administrative hassle of bringing a large number of generators into the system for record keeping purposes. Therefore, a lower waste amount cutoff at approximately 100 kilograms per month is proposed. One hundred kilograms is roughly one half of a 55 gallon drum . . . 220 pounds is about half of a 55 gallon drum.

The disposal facilities regulations, as I mentioned before, are the basis for the Permits and provide design and operating standards for storage, incineration, treatment, and land disposal in its various modes. Another aspect of the facility standards is financial responsibility. This is, again, a new departure from other regulations you may be familiar with. The law requires us to establish standards of financial responsibility for those who want to be in the business of disposing of hazardous wastes. It is as simple as that. Basically, the problem has been that people go into this business accepting wastes for disposal at a price. They collect a lot of money. Then they walk away with the money and leave the wastes for someone else to clean up. This financial responsibility clause is to prevent that type of situation. The Agency intends that people have enough money to adequately close these facilities, and make sure they have some type of liability coverage in case there are accidents. In the case of disposal facilities such as landfills, surface impoundments, etc., we want to make sure that once the facility is closed, it is monitored for 20 years after closure to ensure that the waste is not contaminating surrounding areas. I am sure most of you heard of the Love Canal situation in Niagara Falls, New York where chemical wastes buried 25 years ago have recently come up out of the ground into people's basements and are polluting the area nearby. Over 200 families had to be evacuated from that area. There are histories of birth defects in that community — a very bad situation. This situation clearly points out that wastes do not go away. They are basically contained or not contained as the case may be. We want to make sure that people have enough money to adequately monitor what is happening to these wastes.

Now, all of this sounds very idealistic, but we do provide some flexibility through what we call "notes". You can imagine what the problems have been for EPA. We are trying to define national facility standards that apply across the board to all types of wastes, to all types of industries; at the same time we realize that there are individual situations that require some degree of flexibility in terms of geology, hydrology, and rainfall. There are all types of wastes; there are all types of different combinations of a situation. EPA will have national standards, but we will allow some degree of variance from these standards by these "notes". So, read the "notes" very carefully because they basically establish the criteria for variance from these standards.

There are also limited standards for interim status. There is an interim period after the regulations are final, but before a permit is issued. So, rather than let the whole load of all these regulations fall on people during that initial period, a somewhat limited number of regulations or standards have been specified that apply during that interim status.

Lastly, there are special standards for "special" wastes. These special wastes are of very high volume and a relatively low environmental risk. Flyash, mining wastes, and cement kiln dust belong to this category. Special standards are in effect while we try to sort out what can be done about them.

Media performance standards, in effect, override all of the design and operating standards. Those design and operating standards should provide the necessary degree of environmental protection, but if they do not, the media performance standards override them. These are standards for groundwater protection, surface water protection, and air. They could come into play though they normally would not.

This program, as any new program, has a number of issues associated with it. I mentioned two of them. The small quantity exemption for generators and financial responsibility requirements for disposers. There are others. I think it would be appropriate to address some of the other issues.

One issue is facility availability. There are many people who, basically, are saying "Chicken Little, there will be no facilities available for all of these wastes". Well, what they really mean is that there will be no environmentally-acceptable facilities for these wastes and we accept that. Our estimate is that 90% of all disposal operations will not meet these new requirements. We also do not expect the world to change overnight. We are not going to change the method of operations that each of you have been practicing for over 100 years and just do it with the drop of a steel curtain of regulations. This is provided for, as I mentioned, by the interim status. In other words, everything is going somewhere right now. We realize that. What the interim status provides for is this: If a hazardous waste is reported according to Section 3010 within 90 days and if a permit is applied for as specified in the permit regulations, interim status is automatically granted. A company can continue to do whatever it was

doing until the permit is written. Now given EPA's resources, it could easily be two years before a permit is issued. Meanwhile, this interim status is in effect subject to limited interim standards that I mentioned. Once a permit is issued, there is provision for compliance schedules to meet these new standards which may run upwards to three years. So, what we are really saying is that we are anticipating, approximately, a five-year transition period between what we are doing now and what we want to do (i.e., what will be acceptable as these new regulations go into effect).

The second issue is that there is no provision within RCRA for any federal support for facility construction. There are no construction grant-type provisions in RCRA as there are in the FWPCA.

The third point, which follows from the first two, is that we believe it will fall to the private sector and perhaps to municipalities to construct and operate some of these facilities. The entire Congressional foundation of RCRA is based on the premise, that, given a regulatory program, there is enough capital out there that the private sector will respond and will provide facilities that are necessary. Therefore, there will be no construction grants.

Another issue is the economic impact of these regulations. This is a difficult subject to talk about for several reasons. First of all, the RCRA does not have any reference to economic analysis in it whatsoever. The FWPCA does and the CAA does, but RCRA does not. So, there is some question as to whether it is even legal to consider economics in these regulatory decisions. As you can tell from the scope of what I have discussed regarding this very important new regulatory program, it will impact, simultaneously, practically every sector of American industry. To undertake an economic impact analysis of our entire industrial sector is very difficult. In the Effluent Guidelines Program, for example, where the regulations were tailored to a particular industry, the Agency was able to do a very detailed economic impact analysis for that particular industrial segment. OSW was not able to perform this segment-by-segment analysis, so it initiated the next level up in detail of economic analysis. The public has access to this. What that draft (we have only a draft of the analysis) says for the plating/metal finishing industry is that there is a 75 percent confidence limit that a ten percent closure rate will result because of the full application of those regulations. Now, I want to point that out, because someone mentioned to me that the word was going around that there was going to be a 75 percent closure. What it means is that the confidence level of the analysis is 75 percent that there would be a 10

percent closure. However, another study OSW had done on this indicates that, in the worst case situation, there would be no more than a 2 percent closure. There are two different sets of studies indicating two different results, both of which are "worst case". Therefore, we are conducting a much more detailed economic analysis now and we will provide our results as a part of the final rulemaking package. But, I do mention to you that both the economic impact analysis and the environmental impact statement drafts are available for public scrutiny, and we would certainly like to have your comments on those as well as on the regulations.

Another issue is this consolidated permit that I mentioned to you earlier. Everybody thinks that is a good idea on the surface, but there is some opposition to it. If you have thoughts about the consolidated approach, we would like to hear them too. Last year, the whole issue of state programs was held up because it was not clear. All of what I have said to you so far this morning is, in effect, what would happen if EPA runs this program. States do have the opportunity and it is Congressional intent that states take on this program and operate it. We are not yet sure how many states will seek this authority. We are hopeful that all of them do. To put this into perspective, the NPDES program has 35 states that implement the permit program for water. So that gives you a feel for the split, but we hoping to do a little better. Current estimates are that about 40 states would take on the RCRA program. When discussing consolidation of permit regulations, etc., at the federal level, that does not necessarily mean consolidation at the state level.

One other thing, and I am sure that this will be discussed further by George Thompson and others during this Conference, is the centralized treatment issue. I want to point out one aspect of state regulations impacting on this approach. If a centralized treatment facility is constructed, more likely than not it will be a regional facility that involves interstate transport. As you may know, many states have felt that it is within their power under the Constitution to impose importation limitations or bans on certain types of hazardous wastes. The position runs counter to the whole idea of a regional facility. I think that it is important that industry recognize this and, to the extent that you are at issue, you should enter that debate about importation bans at the state level. There is a lot of commotion and politics involved in conjunction with importation bans, but we believe that they are basically a bad public policy and that we ought to keep open doors so that the wastes can go where they naturally should go.

EPA's Metal Finishing Research Program

George S. Thompson, Jr.*

INTRODUCTION

Why does the Federal EPA conduct research, development, and demonstration activities on the metal finishing industry? How does the Federal EPA establish its research objectives? Today, I will answer these questions, as well as other questions that I feel are pertinent to your interests.

I will start by first telling you who we are. I represent EPA's Office of Research and Development, specifically the Industrial Environmental Research Laboratory in Cincinnati, Ohio. My Branch, the Metals and Inorganic Chemicals Branch, is responsible for conducting RD&D activities on air, water, and solid waste pollution for a variety of industries, including the nonferrous metals industry, the inorganic chemicals industry, the metal finishing and fabrication industry, and a variety of miscellaneous industries such as glass, cement, and asbestos. My Branch, as well as my Director's Division and the Laboratory in Cincinnati, came into existence three years ago as a result of a major reorganization within EPA's Office of Research and Development. The major benefit from this reorganization was the establishment of a new charter directing one research group to address pollution control RD&D for all three of the major pollution media - air, water, and solid waste - for specific industries. Prior to the 1975 reorganization, water RD&D was conducted by one group, air pollution control RD&D by another group, and in most cases these groups of Federal researchers were physically located in different parts of the U.S.

Our broad charter is extremely supportive to conducting valuable research programs; we are one of a small handful of EPA activities that can address the "total pollution problem." Also as a result of our broad charter, we have the capability to interface with other EPA offices and Federal Agencies having regulatory and enforcement responsibilities impacting the industrial sector. Allow me to provide a specific example that directly addresses your interests: my staff interfaces with the regulatory offices, such as the Effluent Guidelines Division, the Office of Solid Waste, the Office of Air Quality Planning and Standards, and EPA's newly structured Office of Toxic Substances; we interface with

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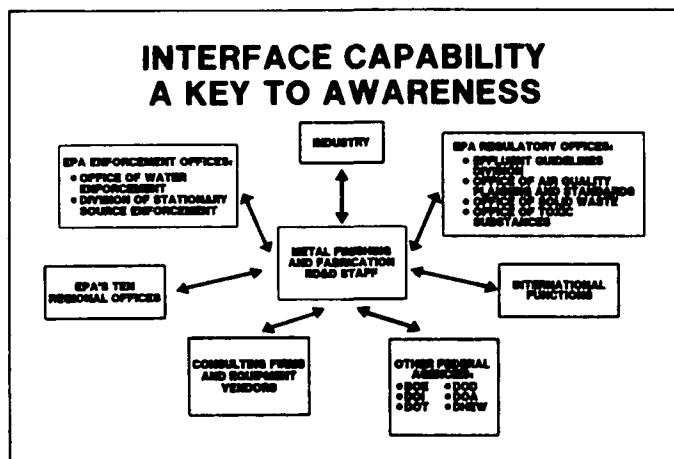
Fig. 1—Interface Capability - A Key to Awareness.

EPA's air and water enforcement offices as well as many of EPA's ten Regional Offices. What does this interface illustrated in Figure 1 provide? Awareness a basic requirement for conducting valuable research and technical support a "must" for establishing firm technical foundations for regulatory and enforcement actions. I must stress the following point: EPA's Office of Research and Development is an independent function within EPA; it does not report through line management to any one EPA regulatory or enforcement activity. If you're asking yourself "what does all of this mean?" - let me summarize. Our interface with these programs, along with our interface with you - the industry, provides us with the awareness to structure our research activities to be best "in tune" with the most important needs (See Figure 2). We in research can develop and implement programs that provide answers to key technically and economically impacting pollution problems.
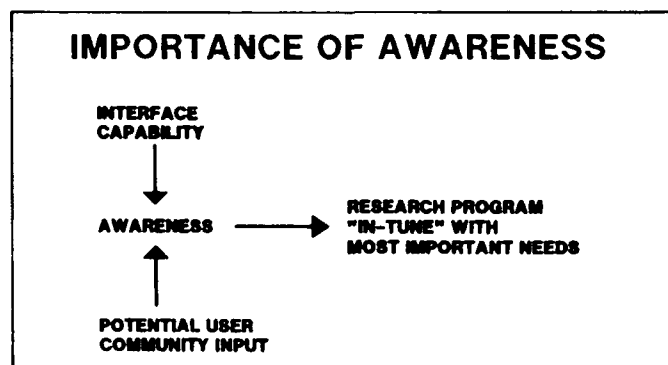
Fig. 2—Importance of Awareness.

MECHANISM FOR CONDUCTING RESEARCH
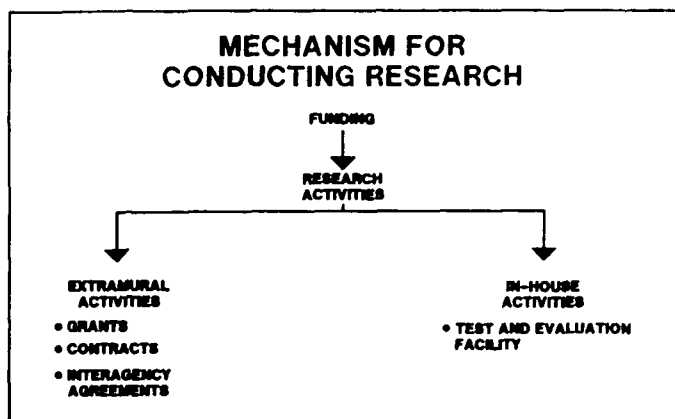
Fig. 3—Mechanisms for Conducting Research.

HOW WE CONDUCT OUR RESEARCH PROGRAM

In the past, our metal finishing research program was entirely "extramural," which means that we conducted all of our research activities through outside organizations by means of three principal mechanisms: grants, contracts, and interagency agreements (See Figure 3). We now have an inhouse research capability a newly constructed research facility in Cincinnati, which we call our "Test and Evaluation Facility." Our research funding is presented to us each fiscal year in the form of Congressional appropriations. We in EPA's research office then allocate these funds to projects based upon our awareness of technological needs. Thus, our awareness to the most important research needs is essential, since we are limited in our funding level.

EPA'S METAL FINISHING RESEARCH PROGRAM

My intention during this presentation is not to provide you with the technical detail of each and every research project in the metal finishing program, but rather to describe the program itself. For your information, I have attached two lists to this presentation: one list provides the title, a brief narrative, and the project officer's name and telephone number for each of the projects comprising the metal finishing program; the second list contains the titles and EPA publication numbers for all of our completed metal finishing projects. If you have any questions or comments regarding the projects or publications as listed, please call or write my office in Cincinnati. I will address the status of several of our key projects during this presentation; several other important projects will be addressed by other speakers in the Conference's remaining sessions.

The metal finishing program is structured around the following goals;

- Advance the state-of-the-art in air, water, and solid waste pollution control and treatment technology.
- Provide EPA with the best technological basis for the setting and enforcing of regulations.
- Provide to the industry the most cost effective

approaches and alternatives for complying to air, water, and solid waste regulations.
- Ensure both EPA and the industry that the abatement of pollution from one media will not result in either pollution to another media or excessive energy consumption.
- Act as a focal point for information dissemination.

These goals are not easily achieved. Everyone must work toward them. We in the Office of Research and Development must have a clear understanding of the metal finishing processes and the resulting air, water, nd solid waste pollutants generated by these processes; we must be perceptive to both the short and long term research needs within EPA and obviously outside of EPA. We rely strongly on ideas, direction toward problems, and expert advice from people like yourselves.

Our pulling together to attempt to reach these goals has allowed my staff to structure the metal finishing research program.

The program itself is broad with many avenues to venture down. Its basis is problem definition and awareness; problem solution is performed through research, development, and demonstration. Dissemination of results, whether positive or negative, is accomplished by means of a variety of mechanisms (See Figure 4).

RESEARCH PROGRAM'S APPROACH
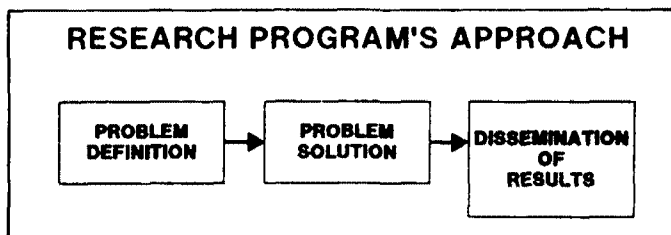
Fig. 4—Research Program's Approach.

Let's first discuss the program's basis problem definition. We are currently attempting to establish a data base on the metal finishing and fabrication industry, which by our definition includes the electroplating and machinery and mechanical products industrial categories established by the Effluent Guidelines Division. One must remember that this industrial definition (detailed in Table 1) includes a large percentage of all U. S. plants that

Table 1
Definition of Metal Finishing & Fabrication Industry

- Electroplating
- Machinery & Mechanical Products
  - Mechanical Products
  - Electrical & Electronic Equipment
  - Photographic Equipment and Supplies*
  - Copper and Copper Alloy Products
  - Porcelain Enameling**
  - Aluminum Forming**
  - Shipbuilding**

* Research in this area conducted by IERL-Ci, Organic Chemical and Products Branch, Cincinnati, OH.

**The current metal finishing research program has insufficient funds to address these areas

11

produces a vast array of products. Three years ago, we inherited an electroplating program from our research predecessors that was directed primarily toward wastewater problems. We initiated and completed a special study to define the air pollutants generated by electroplating operations. Our next "problem definition" activity was started one year ago. Our goal was to design, develop, and utilize a data base containing process information and associated air, water, and solid waste data on the mechanical and electrical and electronics products industries - two of the largest subcategories of the Effluent Guidelines Division's machinery and mechanical products industrial category. We have completed the design of a computerized data base to handle the immense amount of data that we have collected. This data base will serve three primary functions: (1) As a sound technological data base for the development of effluent guidelines and standards, (2) As a prioritizing tool for allowing us to take a broad and complex industry and focus on the most impacting problem areas, and (3) As a starting point for building a data base on other portions of the industrial sector.

The "data base" approach is one form of problem definition - an extremely important approach especially when a limited amount of research dollars is provided for problem solution. Another form of problem definition can be termed "detailed quantification." This term may not make sense, but hopefully after Ken Coulter makes his presentation this afternoon, we will all have a better understanding of its meaning. Ken will describe a proposed research effort between the EPA and the AES that should provide, through "detailed quantification," a clearer understanding of the metal finishing sludge problem. We plan to address this broadly-defined problem area by applying the most acceptable screening tools to quantitatively characterize the hazardous nature of sludges. This screening should then permit us to focus our problem solving attention on those metal finishing sludges having the greatest environmental impact potential.

Key Problem Definition Activities

- Air pollutants from electroplating
- Computerized data base on mechanical and electrical and electronic products
- Planned computerized data base on metal finishing and fabrication
- EPA AES sludge characterization project
- Planned "Awareness Bulletin for Metal Finishing"

Before we complete our discussion on problem definition and its importance to a good research program, I would like to discuss awareness. We are meeting at this three-day conference to become aware of each other's problems and of our progress toward problem solution. We must make each other aware. This conference provides a perfect forum to exchange

viewpoints and knowledge. Your comments on EPA's metal finishing research program are strongly desired.

One last point regarding awareness ... being aware of worldwide advancements in process and pollution control technologies could remedy many of our problems. My office has, for the past 18 months, printed and widely distributed a bimonthly "Awareness Bulletin for Nonferrous Metals." This bulletin is a summary of a major screening of U. S. and international periodicals and publications; it has alerted my staff and members of the nonferrous metals industry to numerous items enabling us to develop and implement a very productive nonferrous metals research program. I plan to initiate an "Awareness Bulletin for Metal Finishing" within the next two months. Please notify my office if you would like to be on its mailing list.

The Research Program's Product - Problem Solution

How does EPA's RD&D program address problem solution? A variety of matrices can be formulated for designing a metal finishing program. Let me describe the one with which I feel most comfortable: The industry, independent of the specific process technology used or product made, can be segmented into three basic scenarios - new plants; existing plants with no air, water, and solid waste pollution control technologies inplace; and existing plants with control and treatment technologies inplace (See Figure 5). Please remember that some of the research activities that I describe overlap scenarios.
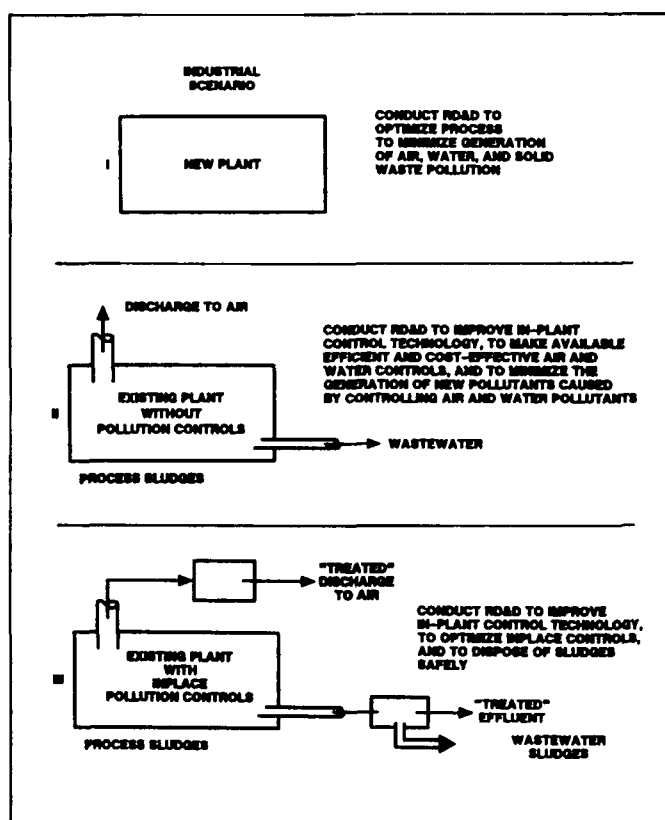

Fig. 5—Matrix Formulation of Plant Scenarios.

Research for New Plants

In the first scenario - new plants - options are available to achieve production and pollution control goals. We conduct research by both evaluating and developing new production processes. Our evaluation project for new processes was described at last year's EPA/AES Conference; this activity with Grumman is still ongoing.

Problem Solving Activities in First Scenario

- New Plants Under Construction -

- New process evaluation program
- New plastics electroplating approach
- New dry circuit board manufacturing process (planned activity)

We are currently developing under contract, a new plastics plating approach and we are planning to investigate a dry circuit board manufacturing process. Are there any new "low polluting" production processes that you can make us aware of?

Research for Existing Plants
Without Installed Pollution Controls

In the second scenario, where the plant has already been built and is fully operational but pollution control and treatment technologies have not been installed, opportunities to provide solutions to pollution problems exist. Even though the production process is inplace, it can still be optimized to cost-effectively minimize the generation of air, water, and solid waste pollutants. Phase 1 of our joint project with the Metal Finishers' Foundation on the demonstration of the HSA Electrochemical Reactor has revealed a variety of inplant changes that can at reasonable cost, be implemented by plant personnel. We are currently documenting the impacts of approximately 50 inplant changes at Varland Metal Services, the host site of our demonstration. Reductions in wastewater flow, pollutant concentrations, and chemical usage have resulted. Some of us feel that pretreatment requirements, in certain situations, can be met or closely approached with implementation of these inplant changes. We hope to prove this in the very near future and possibly prepare a documentary report for broad dissemination on inplant changes, associated costs, and potential impacts.

Phase II, the actual demonstration of the HSA Electrochemical Reactor, is now underway. The first reactor will be installed on Varland's cadmium plating line this month. During March, the second reactor will be installed on a zinc line. Reactors will then be placed on two to three other segregated lines and on the final plant combined effluent. Each reactor will be operated for a six-month period for proper validation. We will disseminate our results to all interested parties as soon as they become available. Our research work on electrodialysis is continuing and John Eisenmann will provide detail during Wednesday morning's session. We have just completed a demonstration of insoluble sulfide precipitation at the Holley Carburetor plant in Tennessee. The results from this demonstration will be published in a pending EPA report; we also decided to prepare a full-color Capsule Report on both soluble and insoluble sulfide precipitation, describing the costs and technical pros and cons of each. Our soluble work is primarily based on part of my Branch's nonferrous metals program; specifically, we are evaluating Sweden's Boliden primary lead and copper smelter sulfide system. We are also currently demonstrating a filtration system for metal-bearing wastewater which I'm sure will be of interest to you; results of this demonstration will be available within the next six months.

A tremendous amount of effort has been placed on reverse osmosis by the AES and EPA's research program. We initiated a "final" R. O. study several months back; we have taken the best membranes, as determined through previous research efforts, skid-mounted them with an evaporator, and placed the system at a plant for detailed evaluation. Our current attention is limited to applying our R. O. skid-mounted system to only one of the three primary wastewater extremes affecting conventional R. O. application. I hope to ultimately address all three extremes: low pH, high pH, and oxidizing solutions. Ken McNulty will report to us during Wednesday morning's session.

When considering existing plants that are faced with a requirement to install wastewater equipment to meet discharge limits, we saw a real need to provide assistance in making the proper technology selection. We have prepared a report that describes "off-the-shelf" wastewater technologies, their pros and cons, and their capital and estimated installed and operating costs, as well as a description of "emerging" wastewater technologies. This report requires one more review prior to publication and broad dissemination - your preview. This afternoon, Clarency Roy will explain how you can help us.

Key Problem Solving Activities in Second Scenario
- Existing Plants Without Pollution Controls -

- Inplant changes (Phase 1 of HSA Reactor Demo)
- HSA reactor demonstration
- Electrodialysis RD&D
- Sulfide precipitation activities
- Filtration system demo
- Final reverse osmosis project
- Technology/cost report
- Solvent degreaser evaluation
- Surfactant scrubbing
- Gas recirculation for VOC control

Our metal finishing air pollution research program was described at last year's EPA AES Conference. Progress has been made. Chuck Darvin and PEDCo's Dick

Gerstle will describe the up-to-date results from their solvent degreaser evaluation program during Wednesday afternoon's session. Research on surfactant scrubbing has also progressed and we are currently evaluating sites for a pilot demonstration. Our plans to demonstrate process offgas recirculation, for volatile organic compound (VOC) control and energy utilization, have not been implemented during the past year, but our work in this area will start shortly.

Existing Plants With Pollution Controls Installed

The third scenario existing plants with inplace pollution controls is the most difficult of the three scenarios to address, but possibly one of the most beneficial. Consider a plant that installed a wastewater treatment facility several years ago that now proves inadequate due to such factors as plant production expansion, new product lines, or more stringent discharge provisions. Must this company "tear out" this equipment and venture into a new "capital intensive" system, which may be one key factor to plant closure? Our approach is to conduct research on optimizing existing inplace systems to possibly prevent this occurance.

I will briefly describe three of our research activities that should provide assistance. The first effort is nearly completed and is being jointly performed by Mitre and Arthur G. McKee. The product will be a manual describing proper design techniques and optimizing approaches for conventional neutralization/precipitation systems. It has been designed for usage by both consultants and plant personnel. Did you ever wonder what effect a change in neutralization chemicals might have on your problem of sludge generation? Let's hope that this manual will provide you with answers to this and similar questions.

The second effort, also planned to be in the form of a manual, addresses inorganic sludges, processes for their dewatering, and methods for their disposal. Funding limitations have prevented us from completing this manual, but we will do our best to get this valuable information completed and out to you.

Key Problem Solving Activities in Third Scenario
- Existing Plants With Inplace Pollution Controls -

- Manual of practice for conventional neutralization, precipitation technology
- Manual on inorganic sludges
- Application of microprocessor technology

Our third primary effort is a novel one. We plan to shortly demonstrate the application of microprocessor technology to minimize effluent pollutant parameter fluctuations, or, in other words, streamline the operation of conventionally-used wastewater treatment systems. How many of you have installed in your plant or know of someone having inplace equipment that allows

excursions to occur? Do these excursions prevent you from achieving your 24-hour max or 30-day average? We have just completed a feasibility study on the microprocessor application. The results of this preliminary study have indicated great potential for solving a "real-world" problem at minimum cost. I solicit your comments on this approach.

Solid Waste Research Program

Before I complete this portion of my presentation, I will describe our solid waste research program. At last year's EPA/AES Conference, many of you made it quite clear that you had a sludge problem. Statements were made, such as "PL 92-500 its forcing us to clean-up our wastewaters, but now we've got all of this sludge! What do we do with it?" We have taken your concerns, and for that matter, EPA concerns, and put together a program. I've already described the EPA/AES sludge characterization project which should point us toward those high priority sludge problems requiring the most immediate research attention. This project is, of course, problem definition.

Our major activity in the sludge area for problem solution came as a result of two separate incidences: (1) Last year's Conference during which our Canadian associates told us of the Federal Republic of Germany's centralized treatment approach and (2) our understanding of the impact of the pending pretreatment and solid waste regulations. Last fall, we evaluated the German centralized treatment approach and its potential in the United States. Paul Minor will describe his findings and observations during this afternoon's solid waste session. We combined our thoughts and formulated our own centralized treatment program. Fred Craig, a member of my staff will provide some detail of this program after Paul Minor's presentation. We have structured our program for broad application across the United States. It focuses on developing and proving out a tool to alleviate the metal finishing industry's potential financial problems associated with compliance to the pretreatment and the solid waste regulations. Please listen closely to what Fred describes this afternoon. He will ask for your comments and suggestions for improvement of our program.

Solid Waste Research Program

- EPA/AES sludge characterization project (planned activity)
- EPA centralized treatment program
  Evaluation of FRG approach
  - Cadmium sludge recycle (planned activity)
  - Polish sludge segregation and metals recovery project (planned activity)

We also plan to initiate a research project on cadmium sludge recycle. We will work with a primary nonferrous smelting company that produces cadmium. This

company will solicit cadmium-bearing sludges from metal finishers to determine if the cadmium values can be economically extracted either pyrometallurgically or hydrometallurgically. If the technology can be worked out, then a new alternative will be available to metal finishers to remedy potential disposal problems with cadmium sludges. Lastly, we are working with the Institute of Precision Mechanics in Warsaw, Poland to initiate a joint international research project on metal finishing sludges. Our research proposal to the Polish investigators calls for a program to develop a centralized containment site for segregated sludges and then to develop and demonstrate inexpensive methods for metals recovery from these sludges. Hopefully, this project will be approved next month for international funding; it could provide valuable results.

I have not described all projects that are ongoing or planned that address air, water, and solid waste pollution control for metal finishing. Please consult the materials attached to my presentation for a complete listing.

HOW CAN WE BENEFIT FROM EACH OTHER?

The metal finishing research program is available for your usage whether you are with EPA or with the industrial sector. We have published reports and are currently addressing problem definition and solution through active projects. We can provide you with more detail on any of these activities if you desire.

If you feel that you have a solution to a metal finishing-related pollution problem and would like to have our assistance in proving out this solution, use the following criteria to determine if we can work together:

1. The problem that you are addressing must not just be your problem. In other words, the more "universal" the problem, the more interest we have.
2. Your proposed solution must have economic merit. We don't want to solve a problem with a solution that's too expensive to adopt.
3. While your proposed solution may solve an air, water, or solid waste problem, your solution should not generate new pollutants or consume excessive energy.
4. Your problem should be one of EPA concern. Our funding is limited and unless we can anticipate a future problem for our regulatory counterparts, we must address solutions to key Agency problems.
5. The time required to develop and demonstrate your solution should be in-line with the timing constraints formed by EPA regulatory and enforcement actions. Obviously, a technological break through five years after a regulation has been established and enforced does not have critical

impact. If your break through could lead to an "ultimate" solution of a key problem, we may still be interested irregardless of timing.
6. Your solution, after being proven out, hopefully would be adopted by your industry and possibly by other groups within the industrial sector. Define potential clients for your solution.
7. Funding required to "prove out" your solution must be within reason. Our resources are limited and are utilized in a very competitive fashion. Your percentage in cost sharing is a very good indicator of your interests.

The normal procedures for us to work together follow:

1. A telephone call or very brief memo to my office that discusses the above criteria is the best way to start.
2. If preliminary interest exists, further discussion, preferably in person, is the next best step for providing additional detail.
3. If a mutual interest exists, your solution "program" could be submitted as a grant proposal or unsolicited proposal for funding.
4. Your submittal is reviewed for relevancy to the Agency's program goals; it is also reviewed for merit by in-house personnel and extramural reviewers, including industry representatives.
5. If reviewers respond favorably, we then determine if your funding needs can be met with our limited resources.
6. If all looks well, we formalize our agreement and work proceeds.

Our normal funding mechanisms with industry are grants and competitive or noncompetitive contracts. There are many complexities associated with funding air vs. water vs. solid waste-related activities; my staff can provide detail to you if you desire.

One last point regarding our working together - you may have a potential solution to a problem that is not relevant to the metal finishing industry, but is relevant to other components of the industrial sector. If this is the case, I have attached to this presentation a list of EPA researchers who have responsibility for specific industrial areas. Please use this list as a starting point for possible joint research and for determining what the specific EPA research program encompasses.

If we do not find the opportunity to work directly together, I solicit your assistance through your expertise. We in the metal finishing research program do not profess to be experts; we are very knowledgeable. You are faced with the "real world" problems that provide you with insight and practical working knowledge. If we can "tap" your insight and expertise to assist us in developing better programs, we will all benefit.

Attachment I
List of Ongoing and Planned Research
Activities for the Metal Finishing Industry

Title	Narrative	Project Officer/Number
Air/Water/Solid Waste Activities:		
Data Base for Metal Finishing Industry	Industry definition; process discussion; air, water, and solid waste generation; control and treatment technology. • Electroplating air emissions have been studied • Mechanical and electrical and electronic products are under study	Charles H. Darvin (513) 684-4491
EPA AES First and Second Conferences On Advanced Pollution Control For Metal Finishers	Conference designed as forum exchange for activities between EPA and industry	George S. Thompson (513) 684-4491
Air Activities:		
Low Solvent Emissions Degreasing Systems Evaluation	Side-by-side comparison of commercially available degreasers with inexpensive modifications for VOC control.	Charles H. Darvin (513) 684-4491
Surfactant Scrubbing Technology for Control of Organic Air Emissions (Planned)	Currently locating site to demo this technology.	Charles H. Darvin (513) 684-4491
Performance of Alternate Coatings in the Environment (PACE)	Evaluation of coatings that should be less VOC polluting. Interagency Agreement with DOT.	Charles H. Darvin (513) 684-4491
Technical Evaluations of Reduced Pollution Corrosion Protection Systems	Evaluations conducted on new commercially - available electroplating and surface coating systems.	Hugh Durham (513) 684-4491
Evaluation of Gas Recirculation System on Paint Bake Oven	Sampling program on auto paint bake oven to determine VOC control and energy reduction gained through gas recirculation.	Charles H. Darvin (513) 684-4491
Development of New Low Polluting High Solids Coating	Interagency Agreement with USAF to develop new aircraft (DOD and commercial) high solids coatings that should reduce VOC emissions.	Charles H. Darvin (513) 684-4491
Water Activities:		
HSA Electrochemical Reactor Demonstration	Demonstration of cost effective (modular in design) wastewater technology. Potential for non-sludge generation. Minimum production loss during hook-up. Minimum plant floor space requirements. • Phase I: Identification and implementation of inplant changes • Phase II: Demonstration of reactor	Ben Smith (513) 684-4491
Documentation of Recycle Reuse Inplant Technologies (Planned)	Planned activity to disseminate inplant technology information to reduce wastewater flow rates, pollutant concentrations, and chemical usage. Recycle reuse research needs defined.	George S. Thompson (513) 684-4491
Wastewater Technologies and Associated Costs for the Small Electroplaters	Report outlining the pros and cons of various wastewater technologies and associated capital and operating costs. Emerging technologies also described. Planned to assist the electroplater in deciding on which technology to use.	George S. Thompson (513) 684-4491
Feasibility Study of Application of Microprocessor Technology for Wastewater Pollution Control	Feasibility of application investigated for variety of industrial wastewaters for purpose of minimizing pollutant parameter excersions. Specific system designed and priced for conventional wastewater electroplating systems (oxidation reduction neutralization precipitation sludge blanket control.)	Ben Smith (513) 684-4491

Title	Narrative	Project Officer/Number
Demonstration of Application of Microprocessor Technology for Wastewater Pollution Control (Planned)	Actual demo on conventional electroplating wastewater system planned. Site for demo currently being selected.	Ben Smith (513) 684-4491
Manual of Practice for Conventional Neutralization/Precipitation Wastewater Systems	Manual designed for usage by consultants and plant engineers for upgrading existing conventional systems and designing new systems. Applicable to all industries treating acidic or alkaline metal-bearing wastewaters (metal finishing, nonferrous metals, inorganic chemicals, etc.)	Alfred B. Craig (513) 684-4491
Demonstration of Microfiltration System for Acidic Metal-Bearing Wastewaters	New filtration system being demonstrated on acidic metal-bearing wastewaters for battery manufacturing plants.	Charles H. Darvin (513) 684-4491
Field Demonstration of New Reverse Osmosis Membranes for Closed-Loop Treatment of Electroplating Rinsewater	Skidmounted system utilizing evaporator and best known membranes operating on high pH (current) and low pH and oxidizing solutions (planned).	Mary Stinson (201) 321-6683
Demonstration of Insoluble Sulfide Precipitation on Metal Finishing Wastewaters	Demo of Sulfex system on metal finishing wastewaters. Final report in preparation.	Mary Stinson (201) 321-6683
Capsule Report: Sulfide Precipitation for Metal Finishers	Full color capsule report being prepared for wide dissemination describing treatability of soluble and insoluble sulfide systems, capital and operating costs, and sludge generation.	Ben Smith (513) 684-4491
Plating Catalysts: A New Technology for Pollution Abatement	New plastics plating approach being developed. Possible substitute for Palladium being introduced.	Mary Stinson (201) 321-6683
Dialysis Purification of Metal Finishing Rinsewater	Demonstration of Donnan Dialysis for recovery of nickel from nickel plating rinsewaters.	Mary Stinson (201) 321-6683
Treatment of Wastewater from Chromium Plating Line	Demonstration of electrodialysis for recovery of chromium from decorative chrome plating.	Mary Stinson (201) 321-6683
Effects of Anions on the Precipitation of Heavy Metal Ions on Electroplating Wastewaters: Phase I	Determination of major interferences in carrying-out conventional treatment.	Mary Stinson (201) 321-6683
Control of Fluoroborates from Electroplating Wastewater	Research to apply electrodialysis to recover fluoroborate reagents from fluoroborate plating rinsewaters.	Mary Stinson (201) 321-5683
Electrolytic Treatment of Oily Wastewaters	New inexpensive technique developed for removing oils from metal finishing wastewater.	Hugh Durham (513) 684-4491
Capsule Report: Evaporators for Metal Finishers	Full color capsule report being prepared for wide dissemination describing the application of evaporators for wastewater control, capital and operating costs, and energy aspects.	Mary Stinson (201) 321-6683
Capsule Report: HSA Electrochemical Reactor Results (Planned)	Full color capsule report being prepared for wide dissemination describing results of HSA demonstration, 3rd party evaluation, and other areas of applicability.	Ben Smith (513) 684-4491
Evaluation of Hydroxide vs. Sulfide Precipitation of Heavy Metals	Side-by-side bench scale comparison of conventional and sulfide precipitation, related costs, and sludge generation.	Hugh Durham (513) 684-4491

Solid Waste Activities/ Centralized Treatment:

Title	Narrative	Project Officer/Number
EPA/AES Solid Waste Characterization Program (Planned)	Matrix of sludges from metal finishing processes will be collected. Variations of Toxicant Extraction Procedure (TEP) will be run on sludge samples. Field studies will be run for comparison.	Alfred B. Craig (513) 684-4491
Centralized Treatment for the Tauton Silver Platers	Feasibility study of centralized treatment by grouping of companies addressing technical and administrative aspects.	Mary Stinson (201) 321-6683

Title	Narrative	Project Officer/Number
Documentation of Federal Republic of Germany's Approach to Centralized Treatment	Report detailing approach used by FRG on variety of industrial liquid and solid wastes.	Alfred B. Craig (513) 684-4491
Capsule Report: Centralized Treatment for Metal Finishers	Full color capsule report being prepared for wide dissemination to discuss FRG's approach to centralized treatment (CT), CT's applicability in U. S., and description of EPA's Metal Finishing Research Program on C. T.	Alfred B. Craig (513) 684-4491
Metal Finishing Research Program on Centralized Treatment (Planned)	Full program to analyze a variety of locales for C. T., detailed analysis of one locale for demonstration of C. T., and development of evaluation tools for determination of applicability of C. T.	Alfred B. Craig (513) 684-4491
Cadmium Recovery from Metal Finishing Sludges (Planned)	Cadmium sludges will be evaluated by nonferrous smelter to determine cost effective method for cadmium recovery from sludges.	Mary Stinson (201) 321-6683
Demonstration of Sludge Segregation and Metals Recovery (Planned)	Planned to be conducted with Polish institute in Warsaw under PL 480 Program. Polish metal finishing industry will prepare and operate segregated collection site for metal finishing sludges. Metal recovery techniques will be developed.	George S. Thompson (513) 684-4491

Report No. *(NTIS No.)*	*Publication Title/General Subject Matter*
12010 EIE 11/68	A State-of-the-Art Review of Metal Finishing Waste Treatment Review of conventional treatment methods. Intended to provide facts for the guidance of the small plater in the selection of a waste treatment process.
12010 EIE 3/71 (PM 215-694)	An Investigation of Techniques for Removal of Chromium from Electroplating Wastes Describes work which was conducted on the removal of hexavalent chromium from plating rinsewaters employing various treatment processes.
12010 EIE 11/71 (PB 208-210)	An Investigation of Techniques for Removal of Cyanide from Electroplating Wastes Describes work which was conducted on the removal of cyanide wastes from plating rinsewaters employing various treatment processes.
12010 DRH 11/71 (PB 208-211)	Ultrathin Membranes for Treating Metal Finishing Effluents by Reverse Osmosis Seventeen different membranes evaluated for the separation of heavy metal ions, acids bases and cyanides from water. Preliminary engineering considerations on the application of reverse osmosis to the treatment and recycle of rinsewaters from an acidic copper sulfate plating bath are included.
EPA-R2-73-287 (PB 231-263)	Investigation of Treating Electroplaters' Cyanide Waste by Electrodialysis The experimental system used in this study was a prototype of a commercial size electrodialysis unit operated continuously under conditions which simulated those of the projected two-stage commercial system.
EPA-R2-73-044 (PB 227-363)	Chemical Treatment of Plating Wastes for Removal of Heavy Metals Chemical rinsing of electroplated parts and batch chemical treatment of spent processing solution is demonstrated as a practical approach for pollution abatement at a small captive metal finishing facility.
EPA-660/2-73-033 (PB 240-722/A5)	New Membranes for Reverse Osmosis Treatment of Metal Finishing Effluents A new membrane designated NS-1 was evaluated for the reverse osmosis treatment of both highly alkaline and acidic (non-oxidizing) metal finishing rinse waters. Preliminary engineering considerations indicated its application in the treatment and recycle of nickel and zinc cyanide electroplating rinse waters.

Report No. *(NTIS No.)*	*Publication Title/General Subject Matter*
EPA-660/2-73-024 (PB 234-447)	Treatment and Recovery of Fluoride Wastes Report presents the development and successful demonstration of laboratory and pilot-scale fluoride treatment techniques for selected aerospace and metal working industry chemical processing solutions and rinse waters resulting from titanium chemical milling, titanium descaling and aluminum deoxidizing operations.
EPA-660/2-73-023 (PB 231-835)	Regeneration of Chromated Aluminum Deoxidizers, Phase I A regeneration process was conceived and tested to reduce the frequency of discharging spent chromated aluminum deoxidizers which are used extensively to deoxidize aluminum surfaces prior to anodizing, conversion coatings, paint preparation, welding and adhesive bonding. Results established that regeneration is feasible, practical and economical.
EPA-670/2-74-008 (PB 223-143)	Metallic Recovery of Wastewaters Utilizing Cementation Bench-scale experiments utilizing the "cementation" reaction (i.e., electrochemical reduction by contact with a metal of higher oxidation potential) were performed for the precipitation of copper and the reduction of hexavalent chromium in industrial streams.
EPA-670/2-74-042 (PB 234-476/AS)	Wastewater Treatment and Reuse in a Metal Finishing Job Shop Describes the complete wastewater treatment system at the S. K. Williams Co. job plating facility. Five integrated waste treatment systems, each for a specific type waste compound are used to protect the rinse waters from process solution drag-out.
EPA-670/2-74-059 (PB 235-588/AS)	Laboratory Study of Continuous Electro-oxidation of Dilute Cyanide Wastes An experimental study was carried out to determine the feasibility of detoxifying dilute cyanide plating wastes by electrooxidation. Cyanide and plating metal concentrations could be reduced to less than 1 ppm.
EPA-650/2-75-019a (PB 243-423/AS)	Source Assessment: Prioritization of Air Pollution from Industrial Surface Coating Operations Report summarizes the results of a program to gather and analyze background information and technical data to establish a data base for the purpose of prioritizing atmospheric emissions from industrial surface coating operations, excluding automobile and architectural painting.

EPA-670/2-75-018   Reclamation of Metal Values from Metal
(PB 242-018/AS)   Finishing Waste Treatment Sludges

Report determines the worth of recovering metal values from metal finishers waste-water treatment sludges. The extraction of metal values from waste sludges by various leaching agents, and the recovery of the metal values by various techniques such as electro-winning, cementation, and liquid - liquid ion exchange were investigated on a bench-scale.

EPA-600/2-75-028   Electrolytic Treatment of Job Shop Metal
(PB 246-560/AS)   Finishing Wastewaters

Full scale in-plant production studies demonstrated the reliability and economics of electrolytic cells containing beds of conductive particles between cathodes and anodes for reduction of hexavalent chromium and oxidation of cyanide in-plating rinse water.

EPA-670/2-75-055   Removal of Chromium from Plating Rinse
(PB 243-370/AS)   Water Using Activated Carbon

Activated carbon is highly effective in adsorbing chromium from rinse water. Laboratory and pilot-scale studies were conducted to determine the effects of basic and acidic media regeneration of chromium-loaded activated carbon especially as it affects adsorption capacity of the carbon after repeated cycling.

EPA-600/2-76-197   New Membranes for Treating Metal Finish-
(PB 265-363/2BE)   ing Effluents by Reverse Osmosis

Long-term reverse osmosis tests showed the NS-100 membrane (formerly NS-1) to be an excellent membrane for potential industrial use in the recycle of rinse water and plating chemicals from acid copper and zinc cyanide electroplating lines. Two experimental NS-101 membranes demonstrated twice the flux of the NS-100 for alkaline zinc cyanide (about 27 l/m^2 hr, or 16 gfd).

EPA-600/2-76-261   Treatment of Electroplating Wastes by
(PB 265-393/9BE)   Reverse Osmosis

Emphasis placed on closed-loop operation with recycle of purified water for rinsing, and return of the plating chemical concentrate to the bath. Three membrane configurations evaluated; tubular (cellulose acetate), spiral-wound (cellulose acetate) and hollow-fiber (polyamide). Test conducted on nine different rinse waters.

EPA-600/2-76-296   Metal Removal and Cyanide Destruction
(PB 266-138/7WP)   in Plating Wastewaters Using Particle Bed
                   Electrodes

A small (0.5 gpm) electrolytic cell consisting of a tin cathode and graphite anode particle bed electrodes and cellophane separator was tested on cadmium and zinc cyanide rinse waters at a plating plant.

EPA-600/2-77-038   Zinc Sludge Recycling After Kastone®
(PB 266-929/9WP)   Treatment of Cyanide Bearing Rinse Water

This report attempts to show the feasibility of zinc metal recovery after oxidation of cyanide by formaldehyde and Kastone®. Included is a critique of the design of necessary equipment and modifications of the plating process needed to accommodate the recovery.

EPA-670/2-77-039   Reverse Osmosis Field Test: Treatment of
(PB 266-919/OWP)   Watts Nickel Rinse Waters

Report presents results of field test data to determine the feasibility of using a poly-amide reverse-osmosis membrane in hollow fiber configuration for closed-loop treatment of rinse water from a Watts-type nickel bath.

EPA-600/2-77-949   Treatment of Metal Finishing Wastes by
(PB 267-284/8WP)   Sulfide Precipitation

Compares conventional lime treatment for precipitating heavy metals present in metal finishing wastes with the ferrous sulfide addition (Sulfex®) process. Studies consisted of jar and bench-scale tests.

EPA-600/2-77-072   Foam Flotation Treatment of Heavy Metals
(PB 267-549/4WP)   and Fluoride Bearing Industrial Wastewaters

Laboratory-scale investigation of floc foam separation techniques to remove toxic heavy metals and fluorides from wastewaters produced at primary aluminum smelters, secondary lead smelters and copper and brass mills.

EPA-600/2-77-105   Ammonium Carbonate Leaching of Metal
(PB 271-014/AS)   Values from Water Treatment Sludges

Experimental studies concentrate on defining an ammoniacal leaching practice that would maximize the return of copper and nickel values from metal-finishing sludges to the leach solution while at the same time minimizing the dissolution of chromium values.

EPA-600 2-77-104   Ozone Treatment of Cyanide Bearing Wastes
(PB 271-015 AS)   A full scale plant demonstration of a highly automated ozonation system for the destruction of cyanide in electroplating wastewaters and for the removal of copper and silver as their oxides.

EPA-600 2-77-099   Inovative Rinse and Recovery System for
(PB 271-298)   Metal Finishing Processes

Report described the feasibility of a non-aqueous rinse and recovery system that can be installed on a plating line. A chrome plating bumper line was simulated for test purposes.

EPA-600/2-77-161
(PB 272-688)

Electrodialysis for Closed Loop Control of Cyanide Rinse Waters

Report evaluates a full-scale, closed-loop electrodialysis system for brass plating cyanide rinse waters. The system proved to be inefficient and therefore unsuitable for this application.

EPA-600/2-77-170
(PB 272-473)

RO Field Tests: Treatment of Copper Cyanide Rinse Water

Report describes results of RO field tests on copper cyanide rinse waters at Whyco Chromium Co. and New England Plating Co. At both sites, closed-loop treatment was used with plating chemicals recycled to the bath and purified water recycled to the rinsing operation.

EPA-600/2-77-194
(PB 272-687)

Regeneration of Chromated Aluminum Deoxidizers - Improved Diaphragm Fabrications and Performance

A laminated ion-selective diaphragm was developed during Phase I (EPA-660/2-73-023) as a necessary part of the electrolytic process. This report describes improved diaphragm fabrication techniques and performance.

EPA-600/2-78-048

Treatment of Fluoride and Nitrate Industrial Wastes Phase II

This report is an extension of EPA-600/2-78-024 laboratory and pilot-scale techniques to treat selected chemical processing solutions and rinse waters containing fluorides and nitrates and the recovery of usable byproducts are described. The results of this study can be used to design a production scale system.

EPA-600/2-78-040
(PB 280-944/AS)

PBI Reverse Osmosis Membrane for Chromium Plating Rinse Water

A laboratory scale research study to assess the potential utility of poeybenzimidazole (PBI) membranes in a reverse osmosis system for the treatment of chromium plating rinse waters. Study demonstrated PBI's chemical stability to withstand long-term contact with chromic acid waste streams.

EPA-600/2-78-011
(PB 280-563/AS)

Removal of Toxic Metals from Metal Finishing Wastewaters by Solvent Extraction

Laboratory-scale investigation to ascertain the feasibility of utilizing solvent extraction techniques to develop economical methods for removing cadmium, chromium, copper, nickel, and zinc ions from metal finishing wastewater.

EPA-600/2-78-085
(PB 283-792/AS)

Removal of Heavy Metals from Industrial Wastewaters Using Insoluble Starch Xanthate

Report describes the preparation of an agriculturally based material and its use in heavy metal cation removal from industrial wastewaters. Insoluble starch xanthate (ISX) was prepared and evaluated in wastewaters from printed circuit industries, lead battery companies, and a brass mill.

EPA-600/2-78-119
(PB 284-097/AS)

Evaporative Process for Treatment of Phosphate Containing Effluent

Report describes the performance and reliability of a pilot-scale evaporative process for the treatment of dilute phosphate containing effluent from an aluminum coil cleaning operation at Alcoa's Warrick County Indiana Plant.

EPA-600/2-78-127
(PB 285-434/AS)

Evaporative Recovery of Chromium Plating Rinse Waters

Report describes the methodology and determines the economics of a new evaporative approach for recovering chromium from metal finishing rinse waters in a typical chrome job shop. Design centered around Corning's PCR-60 vacuum climing-film evaporator.

EPA-600/2-78-130
(PB 286-210/AS)

Aircraft Industry Wastewater Recycling

Report describes the feasibility of recycling certain categories of water used in an airplane factory. Based on the experiences of constructing and operating the pilot-scale plant, an estimate was developed for the cost of a full-scale water recycling plant.

EPA-670/2-75-029
(PB 241-822/AS)

Copper Recovery from Brass Mill Discharge by Cementation with Scrap Iron

Report presents the results of studies of copper recovery and incidental simultaneous reduction of hexavalent chromium in a brass mill discharge.

EPA-670/2-75-015
(PB 241-793/AS)

Pilot Plant Optimization of Phosphoric Acid Recovery Process

Report describes the optimization and economic evaluation of an acid regeneration process which permits the recovery of phosphoric acid used in the bright finishing of aluminum.

ATTACHMENT III

INDEX OF
RESEARCH PROGRAMS/CONTACTS
FOR
THE OFFICE OF ENERGY, MINERALS AND INDUSTRY
OFFICE OF RESEARCH AND DEVELOPMENT
DECEMBER 1978

USE OF THIS INDEX

This Index is meant to facilitate person-to-person contact with the appropriate technical individual within OEMI when assistance is desired. The Index provides the Organizational Charts of OEMI and lists research programs/areas, persons to contact, their organizational location and telephone number. The Index will be updated periodically, as appropriate.

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Associate Deputy Assistant Administrator:
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H2	H3	H4	H5
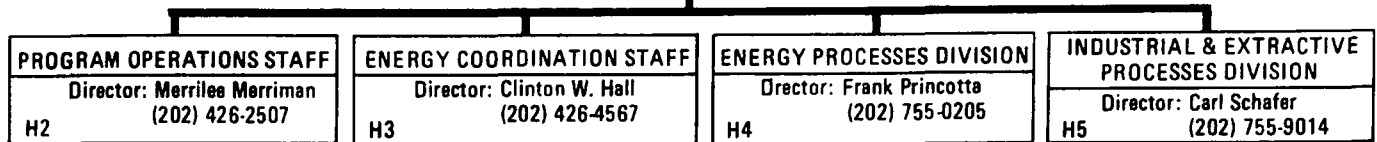
INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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Mr. Everett Plyler R5 629-2915	Mr. Robert Hangebrauck R9 629-2825	Mr. Alfred B. Craig R13 629-2509
Emissions/Effluent Technology Branch Mr. Mike Maxwell R6 629-2578	**Combustion Research Branch** Dr. Joshua Bowen R10 629-2470	**Chemical Processes Branch** Dr. Dale Denny R14 629-2547
Process Technology Branch Mr. Richard Stern R7 629-2915	**Fuel Process Branch** Mr. T. Kelly Janes R11 629-2851	**Process Measurements Branch** Mr. James Dorsey R15 629-2557
Particulate Technology Branch Mr. James Abbott R81 629-2925	**Advanced Process Branch** Mr. P. P. Turner, Jr. R12 629-2825	**Metallurgical Processes Branch** Mr. Norman Plaks R16 629-2733

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Mr. Clyde J. Dial
C2   684-4247

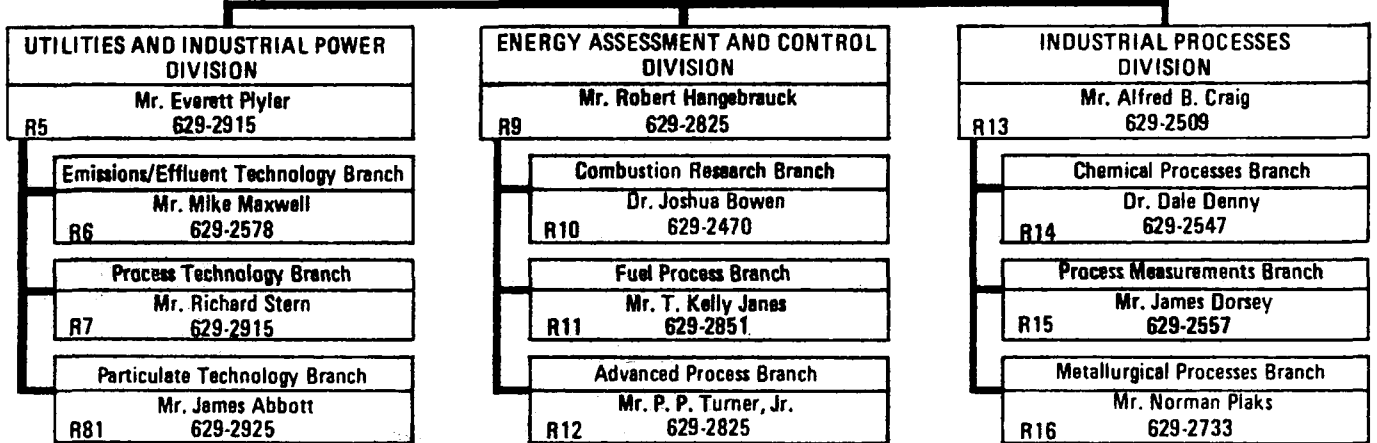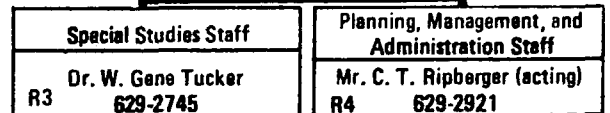| Resource Extraction and Handling Division	Industrial Pollution Control Division	Energy Systems Environmental Control Division
Mr. Ronald D. Hill C3 684-4410	Dr. Eugene E. Berkau C6 684-4314	Mr. Alden G. Christianson C10 684-4207
Oils and Hazardous Materials Spills Branch Mr. Ira Wilder* C4 340-6635	Metals and Inorganic Chemicals Branch Mr. George S. Thompson, Jr. C7 684-4491	Power Technology and Conservation Branch Dr. Harry E. Bostian C11 684-4318
Extraction Technology Branch Mr. Eugene F. Harris C5 684-4417	Organic Chemicals and Products Branch Dr. Irvin A. Jefcoat C8 684-4481	Fuels Technology Branch Mr. George L. Huffman C12 684-4478
	Food and Wood Products Branch Dr. H. Kirk Willard C9 684-4227	

*Industrial Environmental Research Laboratory, Edison, NJ 08817

INDEX OF RESEARCH PROGRAMS/CONTACTS
FOR
THE OFFICE OF ENERGY, MINERALS AND INDUSTRY

Program	Contact	Organizational Location	Phone
Adhesives and Sealants	Ron Turner	C8	684-4481
Advanced Energy Conversion	Bill Cain	C11	684-4335
(e.g. Fuel Cells, MHD, High Temp. Gas Turbines)			
Analytical Procedures — Oil and Hazardous Spills	Mike Gruenfeld	C4	340-6625
Asbestos Manufacturing	Mary Stinson	C7	340-6683
Boilers — Utility/Industrial			
By-Product Marketing	Chuck Chatlynne	R7	629-2915
Effects/Assessment	Wade Ponder	R7	629-2915
Fluidized Bed Combustion	Bruce Henschel	R12	629-2825
NO_x Control (By Combustion Modification)	Josh Bowen	R10	629-2470
(By Flue Gas Treatment)	David Mobley	R7	629-2915
Particulate Control	James Abbott	R8	629-2925
SO_2 Control (Non-Regenerable)	Mike Maxwell	R6	629-2578
(Regenerable)	Dick Stern	R7	629-2915
Thermal Effects Control	Ted Brna	R6	629-2683
Waste Disposal	Julian Jones	R6	629-2489
Water Pollution	Julian Jones	R6	629-2489
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(e.g. Furniture, Printed Products, Transportation Equipment)			
Construction Materials Mining	Jack Hubbard	C5	684-4417
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Energy Management (Conservation)	Bob Mournighan	C11	684-4335
Ferrous Metallurgy	Norm Plaks	R15	629-2733
Fertilizer Manufacturing	Dale Denny	R14	629-2547
Food Products	Ken Dostal	C9	684-4227
Fugitive Emissions Control			
(Call Appropriate Industry Contact)			
Furnaces — Residential/Commercial	Josh Bowen	R10	629-2470
Gas Turbines/IC Engines	Josh Bowen	R10	629-2470
Geothermal Energy	Bob Hartley	C11	684-4334
Glass Manufacturing	Chuck Darvin	C7	684-4491
Hazardous Matrial Spills	Frank Freestone	C4	340-6632
Indoor Air Quality	Bill Cain	C11	684-4335
Industrial Laundries	Chuck Darvin	C7	684-4491
Inorganic Chemicals	Chuck Darvin	C7	684-4491
Iron and Steel Foundries	Norm Plaks	R15	629-2733
Lead Storage Battery Industry	Chuck Darvin	C7	684-4491
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Machinery Producing Industries	Chuck Darvin	C7	684-4491
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General	Jim Dorsey	R16	629-2557
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Mine Drainage (Treatment)	Roger Wilmoth	C5	684-4417
Nonferrous Metals	John Burckle	C7	684-4491
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Mining and Shale Handling/Disposal	Ed Bates	C5	684-4417
Retorting (Surface and Insitu)	George Huffman	C12	684-4478
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Scrubbers	Dennis Drehmel	R8	629-2925
From Specific Sources (call Appropriate Industry Contact)			
Paving and Roofing Materials Manufacturing	Ron Turner	C8	684-4481
Pesticides Manufacturing	Dale Denny	R14	629-2547
Petrochemicals Manufacturing	Dale Denny	R14	629-2547
Petroleum Refineries	Dale Denny	R14	629-2547
Photographic Processing	Ron Turner	C8	684-4481
Pulp, Paper and Wood	Mike Strutz	C9	684-4227
Smelters	John Burckle	C7	684-4491
Soaps and Detergents	Ron Turner	C8	684-4481
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Solar Energy	C.C. Lee	C11	684-4335
Surfactants Manufacturing	Ron Turner	C8	684-4481
Synthetic Fuels from Coal (in Situ)	Bob Thurnau	C12	684-4363
Synthetic Fuels from Noncoal Sources	Tom Powers	C12	684-4363
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Toxic Chemical Incineration			
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Hazardous Materials Spills Related	Ira Wilder	C4	340-6635
Specific Sources (call Appropriate Industry Contact)			
Transportation — Equipment Producing Industries	Chuck Darvin	C7	684-4491
Transportation — Solid Fuels	John Martin	C5	684-4417
Uranium Mining	Jack Hubbard	C5	684-4417
Waste as Fuel			
Co-Firing and Polution Control	Bob Olexsey	C12	684-4363
Pollutant Characterization	Harry Freeman	C12	684-4363
Pyrolysis	Wally Liberick	C12	684-4363

For further assistance on IERL-RTP programs you may contact:	C. T. Ripberger	R4	629-2911
For further assistance on IERL-CINTI programs you may contact:	Clyde Dial	C2	684-4247

Note: for all "684" exchanges, use area code "513"; for all "340 exchanges, use area code "201"; for all "629" exchanges, use area code "919."

Metal Finishing Sludge Disposal; Economic, Legislative and Technical Considerations For 1979

Myron E. Browning, John Kraljic & Gary S. Santini*

The metal finishing industry generates large amounts of sludge. Estimates reveal that by 1983 the U. S. electroplating and surface finishing industry will generate over 1.5 million tons (dry weight) of sludge. At the present time, very limited quantities of sludge are being processed for value recovery or secondary use. Research and development work is under way to reduce the volume of sludge, to lessen the burden of disposal and ultimately to recover valuable natural resources. At the Federal and State levels, regulations to control the generation and disposal of sludges are nearing completion. Many of the questions as to the management of metal finishing waste are still unanswered and some will be addressed during this conference. This presentation will give a brief overview of legislative, economic and technical aspects of sludge disposal.

Considerable progress has been made in regulatory programs at the Federal and State levels to control the disposal of solid wastes. The Federal Solid Waste Disposal Act of 1965 (1) was primarily an authorization for research and development. The purpose of its amendment, the Resource Recovery Act of 1970 (2) was to provide financial assistance to State and local governments for the construction of solid waste disposal facilities, and also to promote research and development. The Act also recommended that guidelines for solid waste disposal, collection and recovery be published in the Federal Register. The guidelines (3) were finally published on August 14, 1974. The guidelines are mandatory only to Federal agencies and apply 1) to all solid waste generated by Federal agencies and 2) to solid wastes generated by non-Federal entities but processed or disposed on Federal property. They do not apply to hazardous waste disposal.

The Resource Conservation and Recovery Act of 1976 (RCRA) (4) not only amended the Solid Waste Disposal Act of 1970 but it greatly expanded the Federal role in the solid waste and resource recovery field. The law requires that EPA develop guidelines to assist state and local governments in solid waste management and approve the state plans for handling of solid waste. A major part of the law is concerned with management of solid waste as it relates to generation, transportation and disposal facilities. EPA is also required to identify what constitutes a hazardous material and provide methods of disposal. Recently the EPA issued the proposed hazardous waste guidelines and regulations covering 1) identification and listing of hazardous waste, 2) standards for generators of waste and 3) standards applicable to management of hazardous waste facilities (5). Hearings on the proposed guidelines and regulations are scheduled for February and March 1979.

Most states have some rules and regulations for hazardous waste disposal. Some states are busy working on laws to control waste disposal while others have the regulations and experience that EPA is using in implementing the mandate of the Resource and Recovery Act. One of the major problems facing the states in this area is the location of acceptable new sites for solid waste disposal.

The State of New York now has two certified hazardous waste receiving landfills and both of these are located in the Buffalo area. The work is in progress to approve a third site before the RCRA regulations are promulgated (6). Costs of having sludge shipped to this western area will create an increasing economic problem with the metal finishers in this state.

In the State of Ohio, disposal of hazardous waste on some 10 or 12 landfills is controlled by state law (7). Sludges are buried separately in geologically secure (clay base) area of the landfill; no manifest is currently required for dumping. It is proposed that metal hydroxide sludge delivered for permanent storage be dewatered to no less than 30 percent solid, excluding water of hydration.

The State of Illinois has three divisions of state government involved in solid waste management: 1) the Illinois Institute for Environmental Quality (IIEQ), 2) the Illinois Environmental Protection Agency and 3) the Illinois Pollution Control Agency. The Illinois Institute for Environmental Quality studies the effects and new problems in solid waste. The Illinois Environmental Protection Agency sets the regulations while the Illinois Pollution Control Agency enforces them (8). Metal

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finishing wastes come under the law which permits a maximum of 200 ppm of any heavy metal and a maximum of 50 ppm of cyanide to be discharged. Illinois has some 64 approved landfills: 24 in the northern sector, 16 in the central region and 24 in the sourthern area of the state. Special Waste Disposal Permits (GREEN) are presently the documents used to control and monitor the waste being landfilled.

California has perhaps one of the most advanced systems for the disposal of solid waste by any of the high metal finishing industry states. Sites for waste disposal are classified as 1, 2 or 3, depending on material being handled. The class 1 sites, 10 of which reportedly are approved around the state, can only receive hazardous waste materials that includes the metal finishing wastes. The hauler must be registered with the state while the generator of waste must provide a manifest identifying the material and the concentration of each compoenent in the sludge being disposed (9).

Metallic hydroxide sludges which constitute part of the solid waste disposal problem, are generally the product of a chemical or electrochemical treatment of waste streams. For a plating shop doing copper, nickel and chromium plating, the equipment needed to process the waste effluents could include: cyanide destruct, chrome destruct, pH adjustments, clarification and sludge dewatering. The reported capital cost of purchased equipment is as follows:

1. Cyanide Destruct
The cost of a continuous treatment system for cyanides with all of the automatic features such as automatic pH meters, ORP probes, chemical feed pumps, liquid level controllers and alarms, the required tanks and piping for flow rates of 1000 gallons per hour and 2000 gallons per hour has been reported as $47,808 and $55,566 (10).

2. Chrome Destruct
The cost of a continuous treatment system for chromium with all the required automatic features and capable of handline flows of 1000, 2000, and 5000 gallons per hour has been reported as $20,416, $21,538 and $24,003 respectively (10).

3. pH Adjustment
The pH adjustment costs for flow rates of 130, 1,300 and 13,000 gallons per hour have been given as $1,452, $4,921 and $18,855 respectively (9).

4. Clarification
The cost of clarification equipment capable of handling flow rates 10,000, 20,000 and about 41,000 gallons per hour has been given as $71,363, $91,575 and $130,102 (10).

5. Other Costs
Among the additional costs can be listed: installation costs, the cost of sludge dewatering and spill control facilities.
The installation costs are about 50 percent of the investment cost (11).
Sludge dewatering equipment adds 10 to 30 percent

investment costs (11). The cost of spill control containment facilities will range from 10 to 20 percent of the total capital investment (11).

For a system operating 16 hours per day (4,000 hours per year) and a flow of 50 gallons per minute for a stream containing:

Copper	= 45 mg/l	(1.1 lb/hr)
Nickel	= 75 mg/l	(1.9 lb/hr)
Chrome	= 100 mg/l	(2.5 lb/hr)
Cyanide	= 30 mg/l	(0.75 lb/hr)

The operating cost would be (12):

Cyanide treatment	= 0.75 lb/hr × $3.25/lb =	$2.44/hr
Chrome reduction	= 2.5 lb/hr × $0.60/lb =	$1.50/hr
Copper precipitation	= 0.5 lb/hr × $0.10/lb =	$0.05 hr
Nickel precipitation	= 0.5 lb/hr × $0.10/lb =	$0.19/hr
Chrome precipitation	= 2.5 lb/hr × $0.10/lb =	$0.25/hr
Labor	= 2 hr/day at $10.00/hr =	$1.25/hr
Utilities	= 10 HP and water =	$0.30/hr
Sludge disposal	= 6 GPH × $0.40/gal =	$2.40/hr

Total	= $8.38/hr
Yearly cost	= $33,520

Another example of waste water treatment is an electrochemical treatment of cooling water blowdown containing chrome and zinc. The installed cost of a building to house the unit plus auxiliary equipment which includes surge tank, lamella clarifier, centrifuge, sand filters and interconnecting piping was approximately $398,000 (13). The Electrochemical Chromate Removal System-Process Diagram is shown below.

Electrochemical Chromate Removal System-Process Diagram
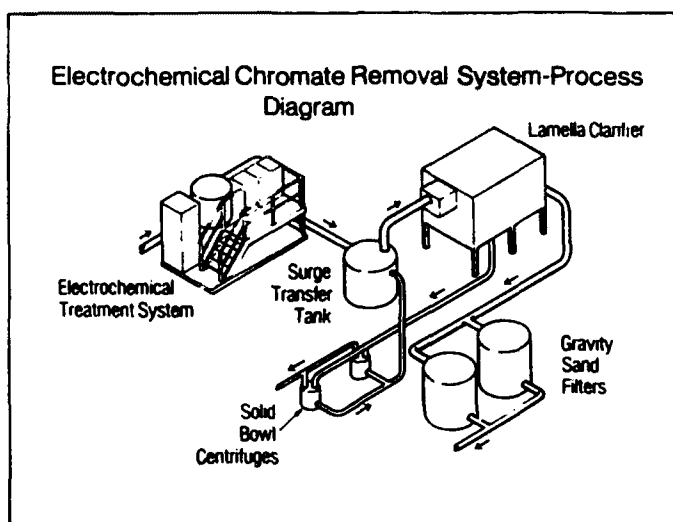
This system is capable of treating up to 600 gallons per minute of cooling tower blowdown containing 20 ppm chromate and 3 ppm zinc. The operating costs per day for

a total flow of 428 gpm at a chromate concentration of 18 ppm is as follows:

Normal operating labor	= $30.00
Electrode change labor	= $ 2.00
Electrode consumption	= $58.13
Power consumption	= $ 2.23
Total operating cost	= $92.36 per day

The overall reaction of this system is:

$$0.5 \; Cr_2O_7 + 3 \; Fe \; (OH)_2 + 3.5 \; H_2O \rightarrow Cr(OH)_3 + 3 \; Fe(OH)_3 + OH^-$$
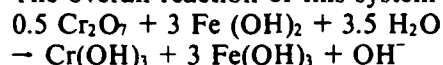
Based on stoichiometry, 3.22 pounds of iron are required to reduce 1 pound of hexavalent chromium. In actual operation 2826 pounds of iron were consumed and 664 pounds of Cr^{+6} reduced, giving a ration of 4.25 pounds of iron per pound of Cr^{+6} reduced. At the electrode cost of $0.3306 per pound, the cost per day for the electrode was $58.13.

Based on the volt and amperes for each cell, 4.8 kwh were consumed for each pound of Cr^{+6} treated. For electrical cost of $0.0112 per kwh and 41.52 pounds of Cr^{+6} treated, the cost per day for power was $2.23.

Operating labor was about 3 hours/day and at a rate of $10 per hour, the cost equated $30 per day.

The system produced about 50 gallons of sludge per day. A contractor removed the sludge to a landfill at 30 cents per gallon or $15 per day.

Sludge Disposal

Public and private landfills are mostly used for sludge disposal. These findings are based on a survey of 600 plating shops. One hundred and fifty companies responded to the questionnaire with 88 of them answering the sludge-related questions. The data are shown in the following table.

Table 1 Sludge Disposal Survey (14)	
Sludge Disposal	*Number of Companies (88)*
Public landfill or dump	32
Private landfill or dump	45
Sell for reclamation	8
Pay to haul away	3

Lagooning has been one of the on-site methods of disposal of metallic hydroxide sludges. There is not much data available as to the effect of this method of disposal on ground water. One may cite, however, one example (14) when a sludge lagoon has been in operation for 10 years and the core borings have shown no measured metal enrichment just a few inches below the sludge layer. These findings, resultant of work done on an EPA contract, could be expected as metallic hydroxide sludges are hard to filter and will rapidly plug any porosity in the soil (14).

Indiscriminate disposal of sludges on municipal landfill also cannot be recommended. Metallic sludges mixed with garbage and organic waste are likely to go back into solution as organic acids are formed through anaerobic decomposition of the organic waste.

It is preferable to segregate the waste and dispose of it in an environmentally safe manner. This practice will minimize potentially toxic elements in the waste from going back into solution. If any problem should arise, the source of the problem can be readily identified and corrective action taken. If it ever becomes economically attractive to recover metal values from a specific type of waste, the location of that waste will be known and it can be readily collected.

Large quantities of metallic hydroxide sludges are being produced. An estimte of heavy metals (copper, nickel, chromium and zinc) in sludge produced in Grand Rapids in 1972-73 and in Waterbury in 1974 has been placed at 1,500,000 lbs and 700,000 lbs respectively. A more recent estimate of total sludge produced from electroplating operations in the U. S. gives the following tons (dry weight) (15):

1974 - 830,000
1973 - 1,200,000
1983 - 1,600,000

Some large metal finishing plants have been reported as spending over $50,000 a year for hauling away sludge valued at about $200,000 (14). It may not be surprising, therefore to learn that a number of schemes have been advanced to recover metal values from metal finishing sludges.

The main problem with metal recovery has been the composition of the sludges. Metals most commonly found in sludge are: copper, nickel, chromium, zinc, cadmium and tin. As indicated in the following table, sludges from various plating lines are not kept separate.

Table 2 Combination of Metals Found in Sludge (14)	
Number of Metals	*Percent of Total (113 Plants)*
1	11.5
2	16.8
3	20.4
4	18.6
5	8.0
6	15.0
7	9.7

According to these data, almost 90 percent of metallic sludges contain two or more elements. The complexity of metallic separation and recovery appears to be related to the number of metals as well as to the type of metal present in the sludge. Segregated sludges can be considered as ready for shipment to a refinery or to a disposal plant. Sludges containing copper plus nickel do not seem to offer great problems in separation. When zinc and/or chromium, however, are present in mixed metallic hydroxide sludges, the separation is neither
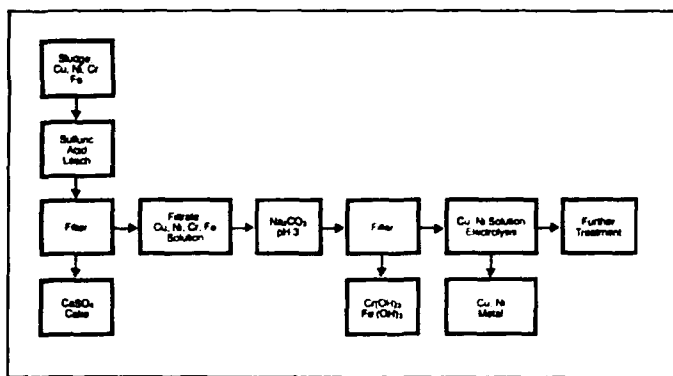
Fig. 1—Recovery of Cu, Ni, Cr, Fe from Mixed Sludge (14).

simple nor economical. A simplified process flow sheet for separation of Cr, Ni, Cu and Fe from a mixed hydroxide sludge can be used to illustrate this point. (See Figure 1).

A more promising way to separate copper and nickel from trivalent chromium is to treat the sludge with ammonium carbonate. In this approach, nickel and copper are extracted while trivalent chromium is left in the residue (14). The cost of ammonium carbonate treatment is considerably higher than that of the sulfuric acid route. Operating costs for a plant processing five tons of sludge per day (dry basis) were estimated at $1,740 per day. The value of recovered metals was placed at $640 per day giving a cost deficit of $1,090 per day (14).

Another concept for recovery of metal values from sludges proposed the following scheme (16):

1. Conversion of dried sludge to chlorides.

2. Separation of metal chlorides by vapor pressure differences.

3. Electrowinning of metals and alloys from a molten chloride bath.

In another process Cr and Fe were extracted and separated from Cu, Ni and Zn by treating the sludge with oxalic acid at pH of 1 to 2. Fe and Cr were precipitated as hydroxides at pH of 9 to 10 and >11 respectively. Insoluble salts such as copper, nickel and zinc oxalates at pH of 11 to 12 change to the hydroxides. Oxalic acid was recovered and recirculated (17). It is claimed that 98 percent of chromium was recovered (18).

In another scheme, ozone was used to separate and recover chromium from mixed sludge (19). Moist sludge was made alkaline with lime and the suspension treated with ozone until trivalent chromium was oxidized to the hexavalent form. The soluble $CaCrO_4$ was then filtered out and separated from the residue.

Nickel has been recovered from sludge formed as nickel sulfate rinses are treated with sodium bicarbonate. Insoluble nickel carbonate precipitate is dewatered by a filter press to 50 percent solids and the dry filter cake shipped to a processing center where it is converted to nickel sulfate plating solution (20). The capital cost to a plating shop involves the purchase of equipment to precipitate and produce a 50 percent solids nickel carbonate sludge. The cost is about $40,000 and the credit that a plating shop owner gets averages 50 percent of the purchase price of new nickel sulfate baths (20).

Recycling of the zinc sludge from cyanide zinc plating has also been reported (21). After adjusting the pH of rinse water to 10.5, proprietary solution was added to treat the cyanide and precipitate zinc as metal oxide. The precipitate after filtration has the solid content of 40 to 50 percent and is returned to the plating tank.

Researchers at the Bureau of Mines (22) have demonstrated that waste phosphate sludges formed during treatment of ferrous surfaces with phosphating solution can be treated to yield trisodium phosphate, zinc and a low-phosphorus ferronickel powder which can be recycled to a steel furnace. Phosphates and metal values were also obtained from phosphate sludge by solvent extraction (23). The sludge was first dissolved in hydrochloric acid. Iron and zinc were extracted with appropriate solvents and trisodium phosphate recovered by crystallization. The value of marketable products was reported as considerably more than the main reagent costs.

Sludges can be disposed of in a potentially environmentally accepted manner by such techniques as heat treatment and chemical fixation or they might be utilized in the manufacture of various products.

Separation of heavy metals in water by an insoluble cross-linked xanthate compound derived from starch is moving out of the laboratory stage. At an estimated cost to manufacture starch xanthate at 20 to 22 cents per pound (24), the initial cost estimates indicate a potential reduction in waste water treatment cost. Even though the metals are said to be reclaimable from starch-xanthate, the starch metal couples may also have to be disposed as a sludge. As the sludge is probably not suited for land disposal as its organic structure is expected to break down and release the metal to the environment, a recently announced sludge recycling technique developed for tannery chromium sludge might work with starch-xanthate sludge. The catalytic molten salt incineration process oxidizes organics in the sludge at temperatures below 1000° F and yields chromium ash. Molten salt incineration system is reported capable of handling 3000 pounds of sludge per hour at an estimated cost of $30 per ton (25).

A batch chemical destruct system, utilizing highly efficient mixing, produces a more granular and less voluminous sludge than the usual hydroxide waste. X-ray diffraction studies of the sludge reportedly reveal a molecular structure less prone to leaching (26).

High temperature heat treatment of sludges at temperature where the metal hydroxides are converted to metal oxides would reduce the volume of the sludge, reduce its solubility and thus reduce the potential of redissolution. The solubility of heat treated plating sludges as a function of temperature is given in Figure 2 (27).

According to the data presented in Figure 2, chemically stable, water insoluble substance is produced at 1100 to 1200° C.

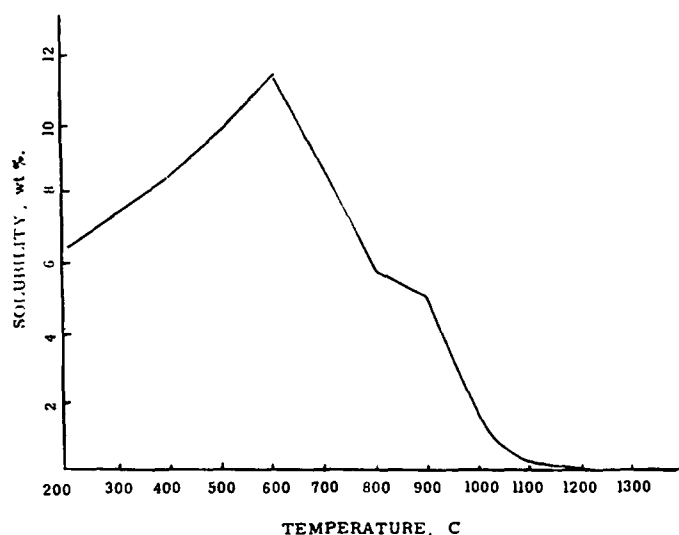Heat treatment of sludges containing chromium has to

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Fig. 2—Water Solubility of a Heat Treated Plating Sludge (27).

be carried out under controlled conditions. If chromium containing sludge is heated above 200° C (392° F) in the presence of alkalies, some of the trivalent chromium is oxidized to the hexavalent form (14, 28). Sludge dried at 200° C (400° F) to 230° C (450° F) in multiple-hearth furnace produced sintered metallic oxides (29).

Some disposal technologies are reportedly environmentally adequate while others utilize the sludge in the manufacture of various products. Among these are listed: 1) land reclamation, and 2) low grade cement. According to one process (30), sludge mixed with proper liquid and solid reagents forms a solid, inert and insoluble material suitable for land reclamation. The stability and chemical properties of the product are given in Table 3 (31):

Ford Motor Company's plant at Lorain, Ohio, has been reported as having used the process on its lagooned metallic hydroxide sludges (32).

More than 70,000,000 gallons of various wastes have been treated. Indications are that the grass grown on chemically fixed waste   waste containing high concentration of toxic metals   does not take up any abnormal metal concentration.

Another potentially beneficial property of chemically

fixed waste is said to be in the ability of the solidified material to remove toxic substances from solutions (33).

According to a recent investigation (34), sludges containing hydroxides of nickel, chromium, zinc, cadmium, copper and aluminum have been found suitable as additives to low grade cement mortars and concrete. Typical applications for the sludge-containing cement mortars has been in the fabrication of flagstones, fences, tiles and road foundations. On a dry basis, the recommended sludge concentration in cement is listed as between 2 and 5 percent. Those cements have improved corrosion resistance and sludge metals cannot readily leach out to contaminate the waters (34).

While research studies suggest these as suitable, the segregation and inventorying procedures mentioned earlier are being recommended more today.

Fluoride containing solutions are used in deoxidizing of aluminum, descaling or pickling of titanium and stainless steel, chemical milling of titanium and in conversion coatings formulations. One of the treatment methods for disposing of fluoride containing solutions is based on lime precipitation. The lime treatment produces calcium fluoride sludge which is disposed as a landfill. As there are some questions raised as to the solubility of calcium fluoride and its eventual leakage into waterways, tests were conducted to establish whether calcium fluoride sludge could be added to concrete. The tests conducted on concrete containing calcium fluoride sludge showed that compression strength of concrete containing 6.8 percent CaF_2 sludge is higher than that of the standard concrete mixture; the flexural strength was equivalent to that for standard concrete. A leachability test showed an insignificant amount of fluoride leaching out of concrete (35).

Landfill disposal is still the most common practice in the plating industry and it will probably be so long as the recovery processes prove to be uneconomical. Segregation of waste streams and sludges, however, could make recovery and other applications for sludges more attractive.

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Table 3 (31)
PROPERTIES OF TREATED AND UNTREATED SLUDGE

Leachate Analysis, ppm

Waste	pH	Solids	Color	Iron	Chromium	Nickel	Copper	Zinc
Untreated Metal Finishing Waste	1.9	30,134	-	8,400	210	160	2,700	21.9
Chemfix Metal Finishing Waste	8.0	300	<5	0.15	0	0.20	0.29	0.15

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The Status of the EPA/AES Solid Waste Program

Kenneth R. Coulter*

The first conference on advanced pollution control for the metal finishing industry was designed in part to develop dialogue between industry and various sections of EPA. This dialogue very clearly pinpointed several problem areas and one of the most serious of these was the disposal of sludges generated from the chemical treatment processes designed for removal of heavy metals from plating effluents.

One of the conclusions of the conference as quoted in the proceedings was "the disposal of residues from wastewater treatment is a continuously growing problem. There is inadequate data to determine the field conditions under which the waste is actually hazardous. Engineering data suitable for designing safe disposal sites is almost non-existent. Much more scientific and engineering effort should be focused in this area."

AES had on several occasions indicated its ability and willingness to call on its large and knowledgeable membership to assist in carrying out a project or projects that would lead to practical solving of some of the waste problems faced by the metal finishing industry.

As a result AES was asked to address itself to the problem of disposal of these wastewater residues and to make a proposal to the Industrial Environmental Research Laboratory of EPA.

A preliminary proposal was prepared and after some modification was presented to the council of delegates at the AES Conference in Washington last June. The essentials of this proposal were that AES resolved that it would:

Co-operate and collaborate with EPA to sample, characterize and code metal finishing sludges from a variety of metal finishing manufacturing processes.

Determine, through a literature review, field studies and dynamic laboratory simulation, conditions under which leachates are likely to be generated for all available methods of disposal.

Co-operate with EPA in working out acceptable test methods and procedures.

The project would be scheduled to be completed within 16 months. The final draft was approved by the AES directors at the end of October and the Proposal was shortly thereafter formally presented to EPA. At the same time the directors approved the mechanics by which the program would be carried through.

A project manager was appointed and Howard Schumacher has been selected to carry out this function. Kenneth R. Coulter was chosen to be Technical Director and a task force of five AES members is being asked to serve as advisors to the project.

A subcontractor, Centec Corporation has been chosen by AES to carry out the sampling and testing procedures.

The function of the Project Manager is to oversee the financial management of the program. He will serve as Liaison Officer to the AES Board of Directors who have ultimate responsibility for the carrying out of the grant project in co-operation with EPA.

The Technical Project Director, in conjunction with the Task Force, will be responsible for the selection of the sites. He will oversee the technical management of the program including test procedures, with the sub-contractor and will consult with the task force when necessary and schedule meetings as required.

The task force will serve as advisor to the technical director. Members will be responsible for their expenses although the project manager may authorize expenditures in special instances.

The sub-contractor will be responsible for conducting appropriate tests, the accumulation of technical data, the preparation of technical reports and all financial documents to meet AES and EPA requirements.

EPA sent the proposal to nearly fifty knowledgeable people both within and outside EPA for comment. These comments are now being digested in Cincinnati and the consensus that will derive from those sources will have considerable bearing on where emphasis is placed within the scope of the project. Similarly AES has been examining their approach to the project and many of the same conclusions have been reached with regard to placement of emphasis.

Every effort will be made to avoid duplication of work being carried out elsewhere in the United States and overseas. Because of a coincidence in timing of arrangements it will be possible to get first hand information from Europe and Japan without the project having to bear the expense of the travel costs.

Continuous communication with the Office of Solid Waste will be maintained, both to provide them with information that may be useful in their determination of the Toxic Extraction Procedure (TEP) and to keep the project on the right track in determining what is deemed to be a hazardous waste. Particularly important will be the solid-liquid ratios used in running the test procedures. The first phase, the characterization of sludges will be

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designed not only to measure the effect of extraction procedures at various pH's, but also to pinpoint the direction to be taken in dynamic laboratory simulation so as to derive the maximum benefit at least cost. This project cannot fill in all the gaps of knowledge on all of the electroplating industry, but it will try to achieve some significant results in a specific part of the problem so that confidence may be placed in its findings.

The success of the whole program will require the co-operation and assistance of the industry, AES and EPA. It is the use of this large source of skills and knowledge, as well as the work of the direct participants that make the attempt practicable and worthwhile. We are confident that this co-operation will be readily available.

Methods and Technologies for Reducing The Generation of Electroplating Sludges

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ABSTRACT

The production of sludge by wastewater treatment systems is of mounting National concern. The safe disposal of these residues is the subject of continuing study and controversy. Under these circumstances, it is prudent to minimize or reduce the production of these materials. A variety of techniques to reduce sludge volume and/or mass are presented in this paper.

Chemical conservation, water conservation, still and dump control, chemical recovery, production equipment selection, treatment system design, reagent selection, and sludge dewatering techniques will be discussed, as they pertain to sludge production. Also included will be discussions on practices that are detrimental to sludge management and production.

Chemical Conservation

An obvious answer to the problem of excessive sludge production is to reduce the quantity of metals entering the effluent stream. There are several ways to accomplish this objective, but the best one is to start at the source, where possible, and reduce bath concentrations. Perhaps the most dramatic trend in this regard is in the strength of chromium plating baths. Fifteen years ago it was not uncommon for platers to use bath concentrations with 40 to 50 ounces per gallon, while today, concentrations in the 20 to 30 ounces per gallon range are most often seen. Those platers using the more concentrated baths should immediately investigate the feasibility of changing to more dilute solutions. This same philosophy should pertain to every plating bath. In almost every plating tank using soluble metal anodes, the majority of the plating solution winds up in the rinse tanks and down the drain. The old rule of thumb in nickel plating is that the anodes go on the work while the plating salts are lost as drag-out. It follows that if plating solutions are more dilute, less metal salts will be dragged out in a given period of time or per unit of work processed and sludge volumes will be reduced proportionately.

The suppliers of proprietary plating baths should be encouraged to develop and promote even more dilute baths than are presently available. While this objective may appear to be contrary to the best interest of the supplier, it certainly beats losing customers to attrition from pollution treatment costs, inflationary metal and manufacturing costs, and the general pressures that tend to tax the endurance of small- and medium-sized

businesses. The money they save in reduced production and pollution treatment costs will remain within the company for the most part and be spent in other productive ways in which the supplier can participate. New manufacturing methods and new production equipment, modernization of old facilities, automation of old lines and general expansion programs will work to the benefit of both the customer and the supplier, and should not be inhibited by a supplier's concern for the future of an old product. Times are changing and the pressures for some changes are inexhorable. Metal and fuel supplies are dwindling and the suppliers must do their part to meet the challenge.

By the same token, the platers can not persist in their bad habits either. Sloppy plating room practices and outmoded finishing methods are everywhere. They are accepted with the explanation that it is the way we have always done it. Or, we have been doing it that way ever since the war (it seems that America only fought one war). It is time for the platers and metal finishers to make an effort to help themselves. Plating shops do not have to be hell-holes. Many plating shops have grown like Topsey and they look it. Plumbing is old and make-shift; the old is mixed with the new. Older tanks in the line have turned to rust, held together with paint (reinforced rust) and tank failure is accepted as the cost of doing business. The topsey-turvy, zig zag work flow encourages floor spills and dribbles. If the average plant manager or owner knew dollar value of chemicals lost on the floor of his shop, he would put a stop to a large part of it. Some dribbles can not be avoided and shop floors will always be wet; but they do not have to be ankle deep in blue, green, orange and grey solutions. When the concrete floor is fizzing like the well known stomach remedy, you have to believe that there is room for improvement, not

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accept it with a chuckle as a way of life. Attitudes will be important, but first the people have to have something to work with.

In hand lines the tank layout should be rearranged to coincide with work flow. Then, rest bars should be installed over the process tanks and even over rinse tanks. These measures will produce less floor contaminants that ultimately are converted to sludge, and also conserve chemicals. The complaint has been made that rest bars slow production, while allowing racks to drain. It should be noted that as much time (and more labor) is expended in carrying work back and forth in the plating room than allowing it to drain properly. Drain boards between tanks keep solutions off the floor and in the process tank.

Archaic and wasteful practices must be eliminated. Such extravagances as cleaning, stripping and phosphating in oblique barrels have no place in modern production methods. The waste in dollars and chemicals is unbelievable, the sludge produced, mountainous. In one plant $50,000 worth of chemicals are used to tumble phosphate work that should be done for $2,000 by modern methods. The phosphate level in the effluent plays havoc with settling and no amount of polyelectrolyte can correct the condition. Tons of coagulants must be added to precipitate the phosphate and create huge amounts of sludge. Every plater must examine his own activities and eliminate those practices that resemble the example described.

Another aspect of chemical conservation that deserves attention is the topic of spills and dumps. Spills were mentioned previously in connection with the condition of plating room equipment. Accidental or deliberate release of large volumes of strong process solutions have, to say the least, a disruptive effect upon waste treatment systems. Dumps can be managed, but spills are seldom caught and treated properly. In any case, these two events make a considerable contribution to sludge production. Spills are unnecessary and must be stopped through preventative maintenance, replacement of marginal tanks, constant concern and vigilance. Dumps can be managed by slowly trickle feeding these solutions into the appropriate point in the waste treatment system. This practice will minimize consequential sludge production but not eliminate it.

The plater and the companies involved in finishing must examine their own dump practices on a tank by tank basis. Many dumps are unnecessary, made through habit like a Saturday bath. Others say they would rather dump a tank than risk reject. Experimenting with extending dump schedules could lead to problems with the quality control people or hell raising from the boss or a big customer. The risk is worth the effort. Any dump that is extended or avoided has economic justification plus the benefit of minimizing sludge production. Work at it. Basically, baths are dumped because of exhaustion (presumed) or contamination. Filtering, skimming and corrective additives are useful in many cases. Better housekeeping, rack maintenance, and avoiding cross contamination resulting from transporting dripping barrels and racks over tanks that are incompatable will help reduce dumps. Suppliers could help the situation by developing formulations that last longer and additions that correct contaminated baths.

Water Conservation

The matter of water usage and its impact upon sludge production may not be immediately obvious. consider that the wastewater treatment system that uses a lime slurry to neutralize acids normally operates with a set point pH in the 9 to 9.5 range. When tap water with a pH near 7 flows through the system, it demands the addition of lime. In actual practice, the effect of dilution is not as dramatic as in the plain water case, but it still prevails, and causes an unnecessary addition to the sludge burden.

Similarly, an increasing number of treatment systems add coagulating agents, such as calcium chloride, ferric chloride, and aluminum chloride. Normally, addition of these materials is made by flow pacing. Thus as the flow increases, the reagent addition increases. If the flows are dilute, the same condition can prevail as in the lime situation and sludge produced unnecessarily.

With water usage now implicated in the matter of unnecessary sludge production, it is incumbent upon the plater to conserve water. Volumes have been written on this subject, but some of the more significant methods bear repeating. Counterflow rinsing is without a doubt, the most important and universally applicable conservation method. Flow restrictors and combination flow restrictor-aerators produce dramatic flow reductions with minimal investment. Aeration with plant air or inexpensive compressors on critical rinse tanks produce better rinsing with less water. Single tank spray rinsing and counter flow spray rinsing are extremely important conservation methods and deserve much wider application. Conductivity controllers work well in rinse tanks that have sufficient recovery time to allow the device to function, such as low production hand lines. Foot operated valves and flow actuated timer valves should be installed on idle rinse tanks.

Chemical Recovery

The prospect of recovering metal and chemical values is well known to most metal finishers, and needs little introduction here. A variety of technology is available to accomplish this objective. Perhaps the simplest and most overlooked recovery method is direct dragout recovery. A still rinse following the plating tank serves to collect the concentrated process solutions carried in or on the parts, racks, or barrels. Periodically, the strong solution in the dragout tank is returned to the plating tank. Naturally, the volume returned is limited to the volume made available in the process tank by evaporation. Subsequent rinse tanks can be counterflowed to the dragout tank in some cases and the efficiency of the recovery process improved. In fact, with four or five rinse tanks in series, the entire flow can be recovered. As with most other recovery techniques, it is important to obtain maximum rinsing efficiency with a minimum amount of water.

Direct dragout recovery has been automated and is

now commercially available in a number of variations that can accomodate most circumstances prevailing in the plating shop. Recoveries range from 50 to 100%, depending upon the rinse and evaporation rates of the application.

Two membrane recovery systems, reverse osmosis (RO) and electrodialysis (ED) are commercially available; and one technique, Donnan dialysis, is under development. RO has proven its value in a number and variety of plating rinse recoveries. It is proven technology with well defined limitations. Most RO limitations are related to membrane stability, but with intelligent application, satisfactory performance is routinely achieved. While electrodialysis does not have the number or variety of applications that RO enjoys in the plating industry, it is beginning to demonstrate its value in recovery technology. The membrane material may be able to offer greater chemical resistance in certain applications than RO, thus making the two methods potentially complimentary in some plating shops. Distillation has been widely, and successfully, applied to metal-bearing rinses. Most limitations relate to the mechanics of design, materials of construction, cooling and vacuum water requirements, and energy demand. Judicious and intelligent applications will justify its consideration in the recovery scene.

Ion exchange technology has for many years proven it worth to the electroplater. Improved resin and equipment have extended the potentials for the technology. The volumes of regenerant required are sometimes excessive and the resultant solution requires evaporative concentration before it can be returned to the plating tank. It should also be added that on occasion RO and ED can suffer from this same problem.

In an overview of recovery technology, such as presented here, it is appropriate to consider the relative flow capacities. In this respect on a dollar per gallon capital basis, ion exchange has the highest capacity and may be the method of choice in those cases where the possibilities for water conservation are limited by the space available, as in many automatic plating machines. With appropriate water conservation measures, reverse osmosis ranks next in flow versus capital dollars. With limited information ED appears to rank next, while distillation follows in the ranking. It should be noted that on the basis of operating and maintenance costs, ease of operation, chemical resistance, and chemical capacity, these rankings could change. It is therefore important to consider every aspect of each technology before selecting one for a specific application.

Automatic direct dragout recovery requires good water conservation as do most recovery methods; but because the capital costs are so much less than the others, it belongs in a class by itself.

All recovery technology is dependent upon the purity of water used to make up for the volumes of rinse water lost to evaporation. The tap water impurities eventually become concentrated in the plating tank, and can interfere with the process. This fact has often been overlooked, and has led to some of the complaints about contaminant build-up in recovery systems. The problem is easily corrected by small ion exchange column or reverse osmosis units.

System Design

System design can have a important impact upon sludge volumes. Averaging tanks or large effluent collection tanks are often regarded as a luxury in the treatment of metal finishing wastes. There are a number of good reasons for employing the averaging concept, but the fact that averaging can reduce sludge volumes deserve mention here. The composition and pH of metal finishing wastewater tend to fluctuate rapidly. Smaller plating shops may demonstrate greater instability than larger plants. Generally, the composition follows the activities in progress at any given moment. This accounts for the greater uniformity sometimes observed in the larger plants where cleaning rinses tend to off-set pickling, etc. However, almost all discharges show some fluctuation.

Fluctuation in composition and/or pH results in system design requirements to accomodate this condition. In the case of pH, the controls must be responsive to these excursions.

Rapid addition of lime in response to a rapidly falling pH can cause the addition of excess lime, particularly if small mixing tanks are employed. Larger mixing tanks will allow the solid lime to dissolve in the neutralization process. Phosphates, sulfates and fluorides can form insoluble compounds on the surface of the lime particles and suppress particle dissolution. Oils, greases and some organics may have the same effect. While these reactions can be beneficial to the effluent quality, they also contribute to sludge bulk by inhibiting the lime dissolution process. Systems employing sodium hydroxide solutions in the neutralization process do not suffer from the bulk created by lime, but they may require the addition of coagulants to assume the collateral duties of the lime. The use of lime can be expected to produce a sludge volume between three and six times the volumes obtained with sodium hydroxide. It is therefore extremely important to design the treatment system to make the most efficient use of the lime. Averaging of effluent composition is one of the best ways to work toward this goal.

Coagulants are added to the flow to accomplish those activities described for lime. The fact that they are pace-fed requires that they be fed at a rate sufficient to handle peak loadings of phosphates, detergents, oil, greases or other materials requiring their application. Obviously, the application rate could be greatly reduced if the loadings of these materials were more uniform. Here again, averaging of composition prior to treatment, assures minimum dose rates and minimizes the resultant sludge volumes.

Another aspect of system design that has a profound effect upon sludge volumes is the matter of sludge thickening. Almost all systems based upon sedimentation technology produce a liquid sludge of comparable water content, usually in the 98 to 99% range. Disposition of

these residues in an as-is state is becoming increasingly difficult and expensive. Many older systems and almost all new systems have provisions for dewatering these liquids. It is axiomatic that the thicker the sludge, the more effective will be the dewatering. This observation applies to both filters and centrifuges and is probably relevant to sand beds. It follows then, that it is important to present to the dewatering stage, as high a solids content as possible. Sludge thickening can be performed in the settling tank or clarifier, or it can be done as a separate activity. Economics do not favor the latter, but it is still being done in many cases, perhaps because it is a common practice in sanitary treatment systems. Some suppliers have combined settling, sludge thickening, and collecting into a single unit. In one case, where a pressure filter was used for dewatering, it was observed that when the liquid sludge presented to the filter contained 5% solids, the filter cycle was 70 minutes and the sludge cake produced had a 48% solids content. When the same filter had a 2% solids content in the feed, the cycle time was about 2 hours and the solids content of the filter cake was 38%. A similar observation was made in a centrifuge application where the solids content was about 15% in the one case and 22% in the other. These percentages are expressed on a weight basis, and do not reflect their actual effect upon sludge volumes. Most sludge haulers charge on the basis of volumes. Shrinkage of sludge cake volume with increasing solids content is not linear and it is sometimes difficult to justify the drier cake on the basis of volume alone. Specifications for sludge composition in landfills is not very precise at the moment. Usually, the authorities require that the sludge be "non-bleeding" or "suitable for landfill", etc. More specific requirements are expected in the future and the plater is advised to watch this situation as it develops.

The matter of volume versus solids content also influences the selection of dewatering equipment. Generally, sand beds and simple gravity systems will produce a jell-like residue having between 7 and 15% solids. Most centrifuges produce a dewatered product with between 10 and 25% solids, depending upon feed concentration and centrifuge design. Vacuum filtration will produce a sludge having between 15 to 30%, again, depending upon feed rate, filter design and operating conditions. Pressure filters may be expected to produce sludge cakes with between 25 and 50% solids, depending upon the same variables as the other methods. Naturally, the operating pressure is a big factor in the determination of solids content.

Future Considerations

The selection of methods described for reducing the generation of sludge is based on two major considerations—economics (capital costs) and the dimension of the problem. Eventually, on a national basis, metal finishers will face additional pressures, such as those being experienced in some states now; i.e., increased transportation costs for hauling sludge, and the percentage of solids acceptable in sludge being landfilled.

Applicability of the Federal Republic of Germany's Centralized Waste Treatment Approach In the United States

Paul S. Minor and Roger J. Batstone*

INTRODUCTION

This morning we have heard about both the EPA pretreatment regulations and the proposed RCRA requirements related to hazardous wastes. The legislation raises some serious economic questions. The installation of pretreatment technology and the subsequent sludge and/or concentrated waste disposal will create a severe capital and operating cost problem for many electroplaters—perhaps to the point where some smaller manufacturers will be at such a competitive disadvantage that they will not be able to continue in business. In addition, the costs of these controls if not minimized by good engineering and common sense — could have the undesirable effect of adding to the price disadvantage of American products. It certainly appears that the nation must wisely manage the resources to be spent on meeting these regulatory requirements.

The basic reason for the economic disadvantages of the smaller individual plater, of course is the engineering fact related to economics of scale. It is simply more expensive on a cost-per-volume basis to treat small flows in a small treatment plant than it is to treat larger amounts of waste in a scaled-up treatment plant. This is especially true for metal finishing wastes where specialized equipment is required for each type of waste.

These basic facts have always made centralized waste treatment very tempting. In the case of municipal wastewater, regional treatment is a reality in the United States and is strongly encouraged. There are also some very specialized industrial situations where centralized treatment has been successfully applied—and some private centralized treatment systems are certainly in business. However, at this time, centralized treatment of metal finishing wastes has just not developed to the point where it would offer significant relief to the majority of metal finishers.

Probably the best example of the success of centralized treatment of industrial wastes—largely metal finishing—is in the Ruhr Valley in Germany.

The Ruhr Catchment Basin in Northwest Germany is one of the most highly industrialized areas in the world. The hub of this area is Essen, which is the site of the original Krupp Steel and Armament Works. In this area, there are about 200 industrial installations that operate about 1000 plating, anodizing, and nonferrous metal pickling baths. In the early sixties, this area suffered from extensive water pollution with all municipal treatment plants experiencing frequent upsets due to highly concentrated discharges of industrial wastes.

In 1964, the first municipally operated waste treatment installation devoted entirely to industrial wastes was built near the Iserlohn municipal treatment plant. The project was jointly funded by industry and the municipality, and charges were set to make it self-sustaining. All concentrated industrial wastes were required to be either taken to this facility or be sent to other specialized treatment facilities.

Since then, several other private and publicly owned facilities have been installed in the area, and a segregated landfill area has been added. The improvement in the environmental quality of the Ruhr Valley in the last 15 years has been noticed by almost every returning visitor, and it certainly appears that the economic strength of Germany has not been hurt. A presentation on the German centralized treatment concept was made in Canada in 1975* by Norman Roesler, who directs the operation in the Ruhr Valley. This presentation expresses general satisfaction with the concept.

With this experience in mind. the EPA Industrial Environmental Research Laboratory (IERL) contracted with CENTEC Corporation to evaluate the German experience in Essen, as a first step in determining if it would be applicable in the United States and if so, would there be major savings in resources and would there be economic impact.

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*"Organization and Operation of Centralized Plants for the Treatment of Special Wastes from the Metal Finishing Industry," N. Roesler, Department of Sewage Treatment Ruhrverband D-43. Essen, Germany. Presented at Technology Transfer Seminar on Waste Handling Disposal and Recovery in the Metal Finishing Industries, Toronto, Canada. Nov. 12 - 13, 1975.

In this presentation today, I hope to accomplish two objectives:

1. Provide an understanding of how the system works in Germany,
2. Give you a rough idea of the general conditions under which it will be advantageous to metal finishers in the U. S. This will be done by presenting the results of a preliminary economic analysis.

Assumptions for Comparative Preliminary Economics

Operating Labor	- $7.00 per Hour
Maintenance Cost	- 5% of Initial Investment
Depreciation	20% of Initial Investment (annualized)
Interest on Capital	10% of Initial Investment
Electricity	- $.04 per KWH
Overhead	- Assumed to be equal for Both Centralized and Local Treatment
Supervision	Assumed to be equal for Both Centralized and Local Treatment
Capital Cost	Vendor Quotes System
Total Flow Rates	10,000 gal/day to 1,000,000 gal/day Mix - CN 10% - Cr 10% - Neutralization 80%

The following equipment was included in cost estimates:

Chrome Reduction
Reaction Tank
ORP & pH Probes and Monitors
Mixer
Pumps
Miscellaneous Piping and Electrical Equipment

Cyanide Oxidation
Reaction Tank
ORP & pH Probes and Monitors
Mixers
Pumps
Miscellaneous Piping and Electrical Equipment

Neutralization
Reaction Tank
ORP & pH Probes and Monitors
Mixer
Pumps
Miscellaneous Piping and Electrical Equipment

Clarification
Settling Tank
Skimmer
Sludge Pumps
Miscellaneous Piping and Electrical Equipment

Vacuum Filtration
Vacuum Filter
Pump
Miscellaneous Piping and Electrical Equipment

OVERVIEW OF RUHR VALLEY PRACTICE

In 1964, the administrative agency responsible for the water resources of the catchment basin of the Ruhr River (the Ruhrverband) instituted a program to provide treatment for hazardous industrial wastes at a facility located adjacent to the municipal waste treatment works in Iserlohn, Germany. At the same time, a strong effort was instituted to gain control of the disposal of all hazardous industrial wastes being generated in the region. This was accomplished by the encouragement of a waste exchange system and of strong efforts to provide an acceptable disposal mechanism for any type of industrial waste.

The initial centralized system provided for:
- Cyanide destruction
- Hexavalent chromium reduction
- Neutralization
- Clarification
- Sludge concentration

The treatment options were combined with the establishment of a segregated area for the disposal of hydroxide sludges, which as much as possible were kept separate for potential future recovery. The initial plant stored the wastes until it was economical to ship them. The initial funding was obtained from local industries, the municipalities, and a loan from the federal government (which was repaid). It was managed by a Board of Directors consisting of both industrial and governmental representatives.

Since that time, the number of both private and public facilities to treat concentrated industrial wastes has increased to the point where all industrial wastes can be sent to facilities specially designed for their treatment or recovery. Facilities are now available for treatment or recovery of:
- Spent electroplating baths and ion-exchange regenerates
- Chlorinated solvents
- Other organic solvents
- Spent sulfuric pickle liquor (recovery of acid and sale of iron oxide)
- Spent hydrochloric acid pickle liquor
- Oil-water emulsions
- Dilute sludges (concentration and disposal)
- Concentrated sludges (segregated landfill)

The centralized treatment plant receives inquiries regarding any waste from the manufacturer who is referred to a private or public disposal service—or the treatment plant may directly accept the waste. A regular waste pickup service is maintained, similar to that for municipal garbage. All treated effluents from both private and public industrial waste facilities are sent to a municipal treatment system.

The prices for the industrial treatment service are such that all systems are self-sustaining; in the case of private facilities, they provide a profit. Normal economic forces have forced large facilities (such as chemical plants) to

provide their own treatment in many cases, while smaller facilities use outside treatment. The technology used at these facilities is similar to that utilized in the United States and is readily available for application in the United States.

DESCRIPTION OF ZEA ISERLOHN PLANT

Although there are now numerous centralized facilities, the first was installed in Iserlohn, adjacent to the municipal treatment plant. Figure 1 shows a flow scheme for the Iserlohn Plant. Waste acid and waste alkaline containing cyanide are transported in color-coded containers. The contents from small containers are stored in 30-cubic-meter tanks. No distinction is made between alkaline waste containing cyanide and those free of cyanide. All are treated as if they contained cyanide. Certain pickle liquors and baths containing nickel and copper are kept separate because the nickel and copper occasionally are sold to a nearby recovery plant which, through electrodeposition, recovers the metals. As much of the pickle liquors as possible is transferred to municipal plants for use as flocculating agents.

The cyanide destruction operates semicontinuously in three phases. In the first phase, the treatment tank is partially filled with sodium hypochlorite and caustic solution. The alkaline waste with the cyanide is added slowly. During this step, the system is not on oxidation-reduction potential (ORP) control. In the second phase, the solution goes on ORP control for final adjustments. The third phase is final pH adjustment.

Acid wastes also are stored in 30-cubic-meter tanks until a sufficient amount is accumulated. The chromate-containing acids go to a reaction vessel where ferrous chloride is added as a reducing agent. The effluent from the acid neutralization, chromate reduction, and cyanide destruct go to a further reaction vessel where lime is added for final pH control. From the neutralization vessel, the effluent travels to what was intended to be a clarifier, but because of problems with floating solids, it is

essentially operated as a solids-separation vessel in which floating solids are skimmed. The mid-level discharge from the vessel goes to one of three rectangular clarifiers, which are arranged to be operated in parallel but which, in reality, operate only one at a time. A breakthrough of material in one of these clarifiers thus can be valved off. One is normally kept empty. The overflow from the clarifiers is pumped to the municipal treatment system. The sludge underflow at about 2 to 3 percent solids, passes to a filter press where it is dewatered to about 35 to 45 percent.

The filter press was originally small, but because of increased sludge dewatering demand, a new, larger press was installed. Salt corrosion was an initial problem, but has been solved by the use of plastic-coated cast iron. The dewatered sludge then goes to a segregated landfill (to be described shortly).

Waste storage vessels are color coded: red or orange indicate acid, blue indicates alkaline. Occasionally acid was mistakenly added to the alkaline solution. In one instance, enough heat was generated to cause sagging in a portion of the plastic vent piping. The acid containers come in sizes up to one cubic meter. Above that size, tank trucks are used. Since the plant will accept concentrated plating baths, no concentrated plating baths are discharged to the sewer. The plant also will accept neutralized and detoxified plating bath and rinsewater if sufficiently concentrated. Neutralized wastes are directed to the clarifiers.

The plant is monitored daily for overflow by the operators; however, the data was not available to us. The laboratory takes a 24-hour composite about once per month. Table I lists the analysis of three of these samples.

At the time of our visit, there had been a malfunction which allowed large amounts of chromic acid into one clarifier basin. This clarifier was isolated for recycling to
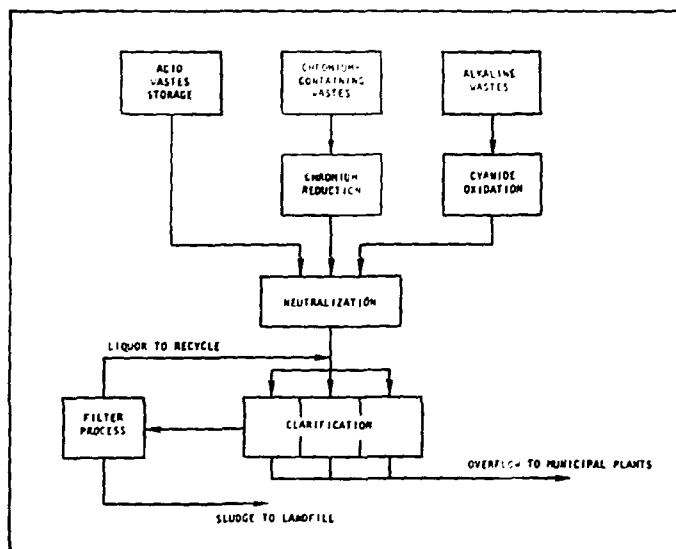

Fig. 1—Flow Schematic for ZEA Iserlohn Plant.

Table I					
24-hour Composite Samples from Zea Iserlohn (All values except pH in mg/l)					
	11/9/78		8/8/78		5/6/78	
Cu	3.2	3.2	5.0	4.1	7.2	7.1
Ni	0.7	0.4	1.0	0.9	1.9	0.9
Zn	1.3	1.2	0.7	0.4	0.6	0.2
Cd	0	0	0	0	0.0	0.0
Cr(T)	0	0	0	0	1.02	
Cr+⁶	0	0	0	0	0.74	
Fe	2.2	0.6	0.67	0.58	2.0	
NH⁴	51		182		583	
Nitrate	1340		1640		3050	
Nitrite	92		62		102	
Cl	5000		12500		1800	
Sulfate	1485		2590		2285	
Conductivity (in Ohms)	12.3		34		12.6	
Cn (total)	18.8		0.33		0.38	
(Cl amenable)	17.6		0.18		0.31	
pH	9.4		7.8		8.3	

treatment. Although the plant was 14 years old, it was reasonably neat and well kept, for being built in 1964. It did not have a significant amoung of automation. The only major control was on ORP for the cyanide destruction. The final pH was generally kept between 9 and 10. They do not monitor pH as closely as is common in the U. S.; there is no continuous pH recorder.

One of the basic goals of the centralized waste treatment plant is to collect small amounts of waste that might have value elsewhere if available in sufficient quantity. Although this function is apparently performed to some extent (in the case of nickel-copper solution), obviously no significant amount of exchange takes place at this site. In further questioning, Mr. Roesler said that the exchange of waste at the plant is not really an extensive portion of the throughput.

The basic media used to accomplish the exchange of chemical waste are a series of newsleters that list desired wastes for sale. These are published weekly by the German equivalent of the Chamber of Commerce. Initially, this list was quite extensive, but over the years, enough contacts had been made so that only a relatively few wastes need be marketed.

One of the keys to the success of the centralized treatment concept was the establishment of a segregated area for hydroxide sludges. The district has established a sludge disposal site for handling hydroxide sludges from any type of metal working plant and is not limited to metal finishers. This facility takes dewatered sludges only, and single-metal sludges are kept separate for possible future recovery. The sludges are deposited on the sides of a deep pit. Any leachate drains to the bottom of the area and is returned to the treatment plant by gravity. Currently, they are not being recycled to any extent, although such sludges are available free from any user. Mr. Roesler said that, occasionally, a manufacturer having need for a certain type of metal will take a small amount of the sludges. At the time of our visit, trucks were continuously dumping hydroxide sludges. There were several different colors of sludge, each kept separate for possible reuse.

Runoff is collected and sent to the waste treatment plant. At the time of our visit, weeds, mosses, and other vegetative plants have established themselves on the hydroxide sludges.

In summary, it can be said that the Iserlohn plant, in itself, does not represent any new technology. It is the application of existing technology that has solved the waste problems of electroplaters in the Essen area.

APPLICABILITY TO THE UNITED STATES

So far we have only heard how the system is working in Germany, as told by some people who are obviously sold on the concept for their particular situation. Of greater interest is its applicability to the United States, taking into account U. S. costs and U. S. environmental requirements. One of the striking aspects of applying

centralized treatment to the mix of industries in any industrial region is the large number of possible configurations. A thorough examination of the economics requires a specific study for the local situation, but in my paper today I am going to try to cover in a general manner areas where it is likely to offer the greatest economies.

When evaluating centralized treatment from an economic viewpoint, you are balancing the decreased capital and plant operating costs resulting from the economics of scale against the transportation costs for delivering the wastes to the centralized treatment plant. If you are going to evaluate the feasibility of centralized waste treatment in a regional area, you must know:

1. The sources of industrial waste.
2. The characteristics of the waste being generated.
3. The technology currently installed in the generating facilities.
4. Special factors that would affect the ability of the manufacturer to become involved in centralized waste treatment.
5. The pretreatment requirements.

The evaluation that I am about to present is based upon several assumptions which, although they may be realistic at this time, are always subject to the winds of change.

Figure 2 shows the effect of centralized treatment on the capital costs that would be allocated to a single plant versus a number of the equivalent plants of identical capacity which could subscribe to centralized treatment. In reality, of course, plants of different capacities would be subscribing; but this figure illustrates the magnitude of capital savings.

The shaded curve covers the normal areas of scale-up for processing equipment. The line drawn in is our estimate of the scale factor for conventional electroplating waste treatment systems. The ordinate is the ratio of costs which would be allocated to a centralized facility to the costs if the plant installed its own system. It is a battery limits comparison. It can be seen that major savings in capital costs occur with as few as 5 to 10 plants participating; and the bulk of the capital
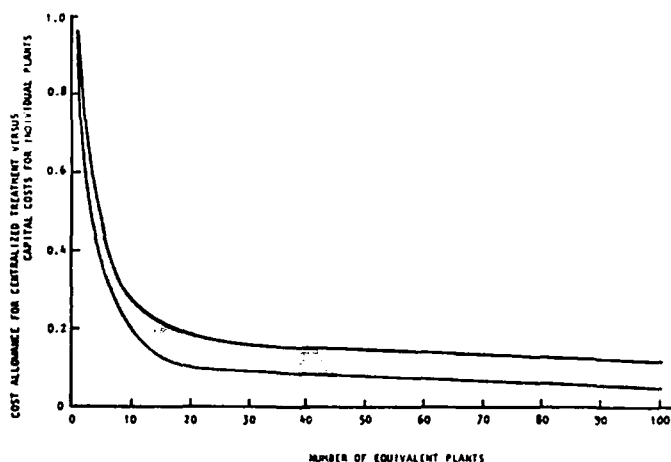

Fig. 2—Effect of Centralized Systems on Capital Costs Per Plant.

savings are realized with 25 plants participating. This is the basic effect of size on capital costs. This type of capital savings in scale-up is well known and does not depend on any significant assumptions.

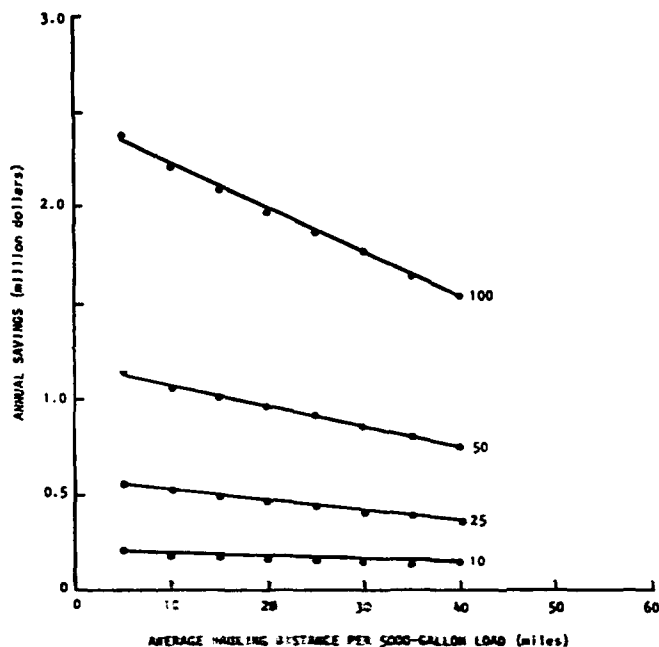Before we can examine the total economics of centralized waste treatment, however, we must provide some assumptions for the necessary questions. In the analysis which follows, we have made the following assumptions.

- BAT for pretreatment will be reduction of waste flow, segregation of wastes and conventional treatment.
- Plants affected have CN, Cr+6, and other metals, and have no control technology currently installed.
- Comparisons are made for battery limit plant additions only.
- Plants will continue to use POTW for wastewaters which meet pretreatment requirements.

The analysis of centralized treatment options is very burdensome without the use of a computer for the calculations—and we have analyzed the effects of different assumptions than these shown—but this presentation is aimed at illustrating the general principles of centralized treatment.

Using these assumptions, the annual savings for threee different plant waste loads as a function of average hauling distance are shown in Figures 3, 4, and 5 for 5,000, 10,000 and 40,000 GPD, respectively.

The number of plants subscribing are shown as parameters. The slope of the curves with hauling distance becomes steeper as the basic plant waste load increases. This occurs because at larger waste loads, there is less gain attributed to economics of scale and transportation costs are important. For waste loads of 5 and 10 thousand GPD, considerable savings are available at relatively high hauling distances—while at 40,000 GPD, the break-

Fig. 3—Annual Savings Versus Average Hauling Distance At 5,000 Gallons Per Day.
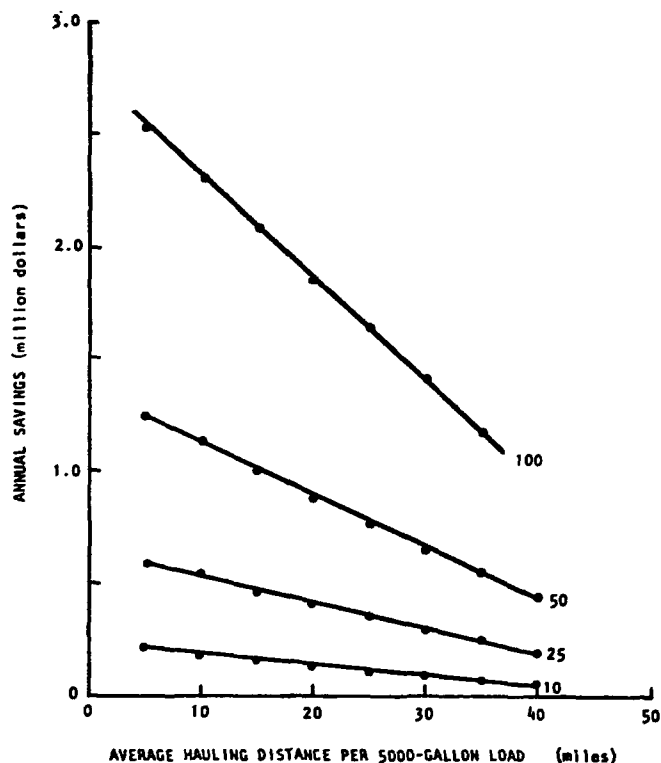
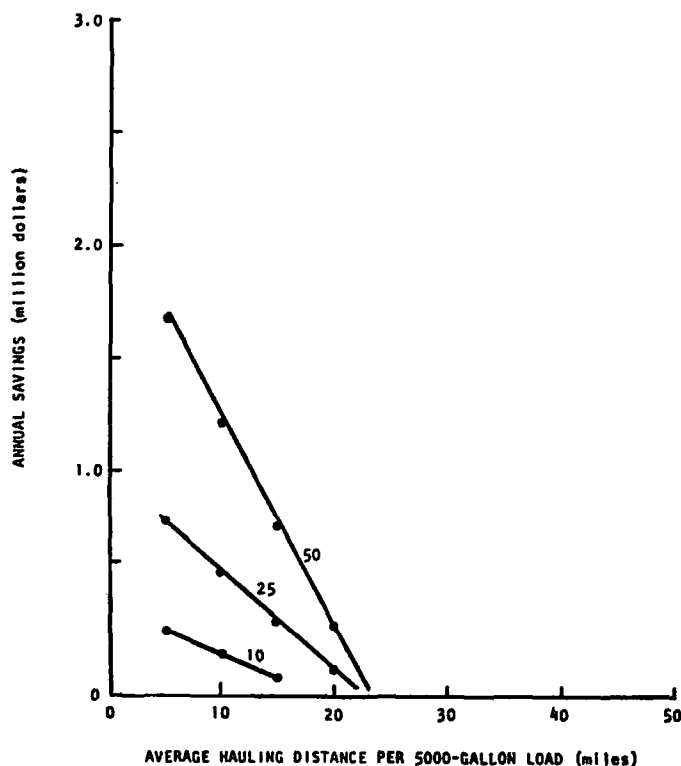Fig. 4—Annual Savings Versus Average Hauling Distance At 10,000 Gallons Per Day.

Fig. 5—Annual Savings Versus Average Hauling Distance At 40,000 Gallons Per Day.
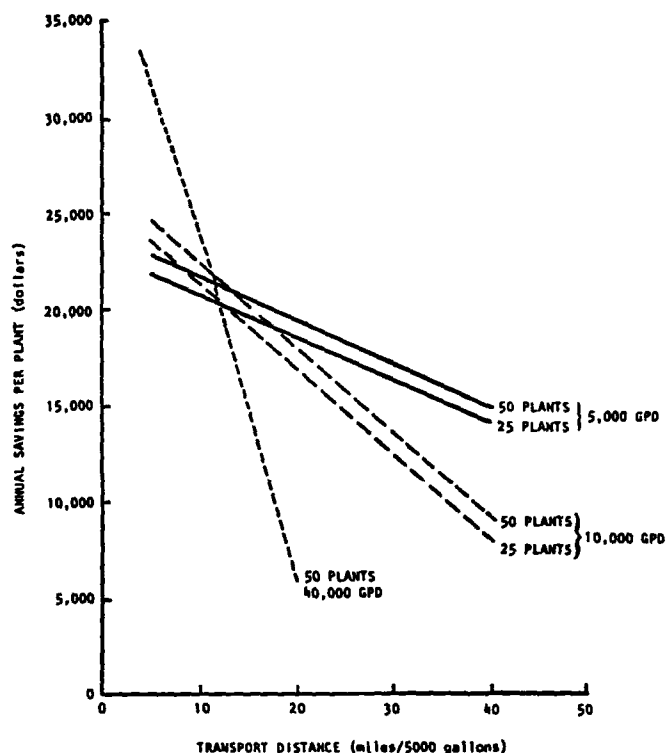
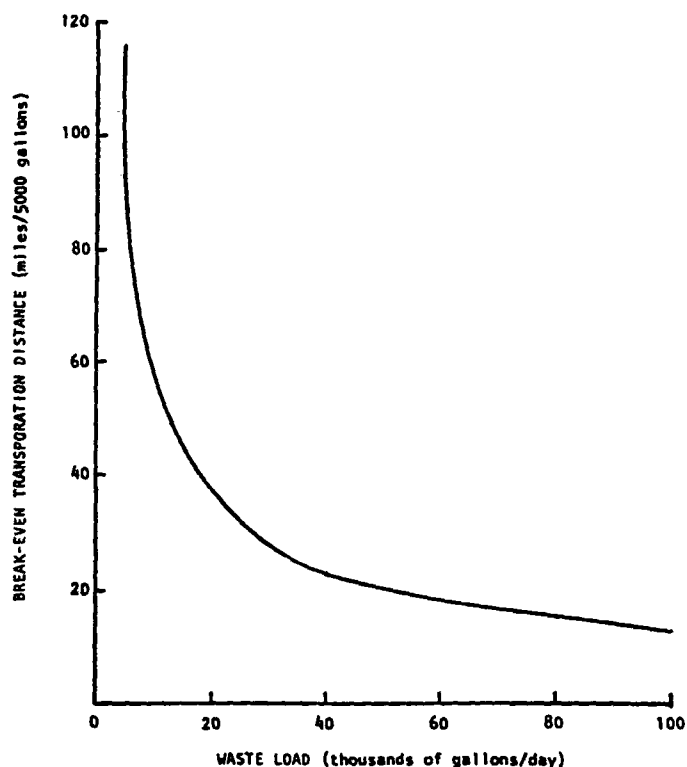Fig. 6—Annual Savings Per Plant Versus Transportation Distance.

Fig. 7—Break-Even Transport Distance Versus Size of Load.

even point occurs at around 20 miles. Figure 6 shows the three capacities on the same graph and gives the results in annual savings per plant rather than total for the region. The increased sensitivity of the savings with hauling distance is shown very clearly in this figure.

Figure 7 illustrates the effect of waste load on the break-even hauling distance for the stated transportation cost—over a wide range of waste loads. The area above the curve might be considered a normally infeasible range. This figure shows the very favorable economics for centralized treatment for smaller waste loads.

Transportation costs are very hard to pin down, since they are dependent on local conditions. In the data shown so far, we have used 90 cents per mile since it is an actual cost for one waste treatment facility leasing a truck. This figure is the average cost for that location and includes the salary of the driver, which is a major cost. The loading time, traffic type, and highway conditions can greatly affect this number.

Figure 8 shows the effect of transportation costs on the annual savings for a specific situation where all the plants are located at 15 miles trucking distance. In the case of a waste load of 40,000 GPD, the break-even point is $1.40 per mile, while the smaller waste loads are relatively insensitive.

Figure 9 shows the effect of transportation costs on the hauling distance break-even point.

In an actual situation, of course, there are plants of various sizes that would choose different options for interacting with the centralized facility. Many plants might choose to treat some wastes selectively where it is most economic to do so, and to send others to a
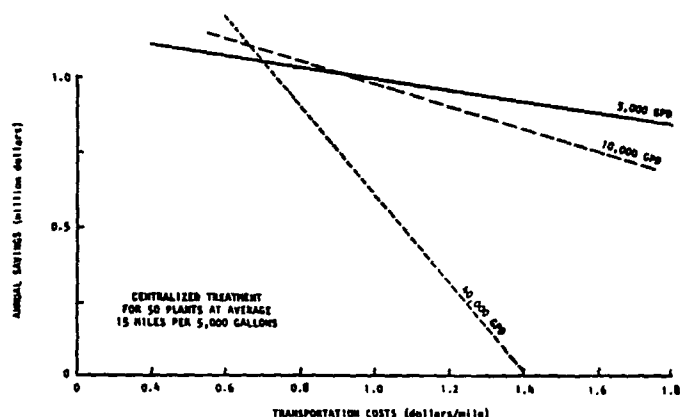

Fig. 8—Effect of Transportation Cost On Annual Savings For Three Plant Waste Loads.
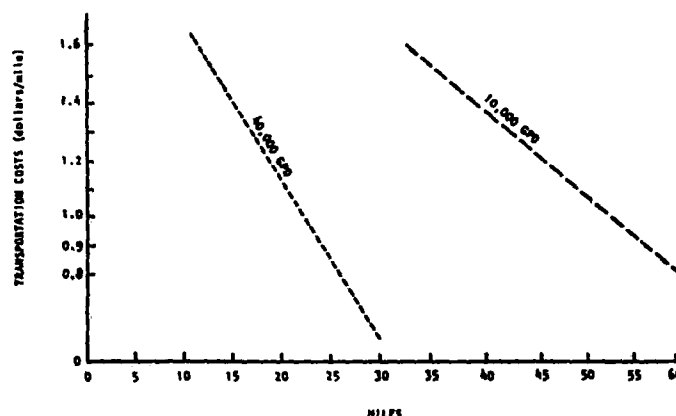

Fig. 9—Effect of Transportation Cost on Break-Even Points.

centralized system. There is considerable room for optimization within the situation of each plant. Thus, in the data presented so far, we have force fit a situation and calculated the savings. In reality, as has happened in Germany, the plants have been given options and have selected the one that best fits their needs. There is also the option of siting several treatment plants so that transportation costs are minimized.

SUMMARY

- Centralized treatment appears to be working very well in Germany.

- There appears to be substantial economic savings for small plants in the United States.

EPA'S Centralized Treatment Program

Alfred B. Craig, Jr.*

Introduction

The Metal Finishing Industry utilizes more than 100 surface finishing and fabricating operatings which require aqueous application and removal of various metals to and from metallic and plastic parts. Contained in metal finishing process baths are various cyanides and cyanide complexes, hexavalent chrome, copper, nickel, zinc, cadmium, and other metals which must be disposed of once the useful life of the bath has been reached. In addition, rinse waters are generated which contain dilute concentrations of these metals resulting from washing of the plated parts.

A vast majority of electroplating shops reside in large industrial communities in and around municipalities. Eighty percent of the plants in the electroplating industry discharge untreated or lightly treated rinse water and plating baths to municipalities for treatment by POTW's. These nonbiodegradable pollutants are discharged in over one billion gallons of process water each day to biological treatment systems, and hence, are ineffectively treated by such systems.

Impacts of Metal Finishing Operations on Publicly Owned Treatment Works (POTW)

Pollutants in metal finishing process wastewater interfere with proper operation of biological systems and restrict the utilization of biological sludges because of their high metal content. Cadmium, chromium, lead, nickel, and zinc are not destroyed when introduced into a POTW and will either pass through the system or contaminate the sewage sludge. The metal content of this sludge may preclude land application of sewage sludge on food crops; questions also arise regarding sewage sludge disposal by incineration due to the volatility of cadmium and lead.

The Enabling Regulations

The Environmental Protection Agency is currently proposing and promulgating a series of industrial wastewater pretreatment regulations. These regulations will reduce the introduction of industrial wastewater pollutant parameters to publicly-owned treatment works

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(POTWs). Indirect dischargers, in complying with these pretreatment regulations, will be required to install various process wastewater control and treatment technologies at their plant sites. Some components of the industrial sector will suffer an economic impact resulting from adoption of these regulations, and some components, comprised of plants small in size with limited personnel and capital for addressing these regulations will undoubtedly be impacted through plant closures.

Simultaneously, EPA is implementing Congress' intent of the Resource Conservation and Recovery Act (RCRA). Industry, in complying with the provisions of RCRA, will be required to safely dispose of their residual wastes. The cost of waste disposal and management will likely increase as will administrative burdens associated with the proposed waste management system.

Prior Research on Centralized Treatment

Two years ago, EPA's Office of Research and Development (ORD), in anticipation of the potential impact to industry resulting from compliance to pending wastewater and solid waste regulations, began investigating conceptual alternatives to on site industrial waste treatment by generators. One alternative showing promise is centralized treatment. Scale of economy and improved waste management are the primary assets of this approach. Centralized treatment provides management and personnel whose expertise lies in handling wastewater and solid waste residuals as a primary responsibility as opposed to production personnel providing intermittent supervision of treatment practices at individual industrial plant sites.

One primary difficulty that ORD encountered in developing a program on centralized treatment was to determine the appropriate administrative technique for implementing this concept. Considered were: (1) companies with similar processes and pollution problems located near each other could group together and construct a centralized treatment facility, (2) private enterprise could construct centralized treatment facilities and market treatment to industry located in its vicinity, and (3) some government organization could establish and manage its own locally controlled treatment facility. The first approach was researched through ORD's Metal and Inorganic Chemicals Branch with a group of established silver platers in the vicinity of Taunton, Massachusetts; scale of economy was proven. The

following program outline establishes an approach for implementation of centralized treatment by both private enterprise [(1) and (2) above] and the public sector.

The Metals and Inorganic Chemicals Branch Program

The Metals and Inorganic Chemicals Branch is developing the procedures to determine, on a case-by-case basis, the feasibility of centralized treatment facilities (CTF) for metal finishing wastes. This plan addresses the usage of the CTF for disposal and management of the following metal finishing wastes:

- Concentrated, metal bearing wastewaters including those containing CN and chrome.
- Metal bearing sludges resulting from application of on-site pretreatment technology.
- Metal bearing sludges resulting from application of on-site direct discharge treatment technology.

As outlined in the following pages, this detailed plan provides:

- Screening feasibility studies for 5 regions with high densities of metal finishing plants (Phase I).
- A detailed study of one region resulting in a comprehensive design of the collection and disposal system (Phase II).
- A demonstration of the system designed in Phase II (Phase III).
- A retrospective analytical evaluation of the demonstration and appropriate dissemination of the results (Phase IV).

The primary output from the first two phases will be the site selection for demonstration and a "blueprint" for construction of a CTF at the selected demonstration site. Detailed activities for each of these four phases is contained in this paper.

This program will:

- Provide EPA and U. S. industry with a cost effective approach to remedy impacts to industry derived from complying with pretreatment regulations and sludge disposal regulations for both industrial pretreaters and direct dischargers.
- Use municipal governments, as a point of contact with local industries, for technology and associated cost information that will enable industry to economically meet regulations.
- Utilize experienced personnel, whether from the private or public sector, to operate CTF's to ensure the long-term control of industrial wastewater discharges and ultimate safe disposal of sludges.
- Provide, through scale of economy, economical treatment of metal finishing wastes withoug hampering potential resource recovery of industrial residues, such as recovery of strategic metals from metal finishing wastewaters and sludges.
- Provide an effective solution to industrial waste disposal in many regions throughout the United

States, and reduce impacts associated with conscientious waste disposal.

Though the program specifically focuses on the metal finishing industry, a widespread, complex industry for which impacts from pretreatment and RCRA regulation implementation are anticipated to be extreme, it will contain latitude to include other industrial categories into subsequent analyses.

PHASE I
DEVELOPMENT OF TOOLS TO AID REGIONS WITH HIGH METAL FINISHING DENSITIES IN DECISIONS CONCERNING CWT AND SELECT AREA FOR CWT DEMONSTRATION

There are four major functions for Phase I:
1. Selecting the regions for case studies.
2. Developing analytical tools and evaluating case studies.
3. Disseminating results of case studies as examples for other groups considering CWT.
4. Selecting one region for system design.

1.1 **Select Regions for Case Study**
The objective of this section is to select 5 regions for case studies. The selection of these regions will be based on screening thirty locations using predetermined selection criteria based on information collected by a broad-brush survey of regions with an adequate density of electroplaters.

1.1.1 **Develop Criteria for Reducing Candidate Sites From Thirty To Five**

A list of recommended criteria used to narrow the number of candidate sites from thirty to five will be developed by reviewing and analyzing project objectives. These criteria will address technical issues such as industrial density and profiles as well as esoteric issues such as the political climate of in-phase regulations affecting CWT.

1.1.2 **Development of Data Base on Candidate Regions**

Each of the regions will be profiled regarding its industrial community and municipal ordinances through the use of Dunn and Bradstreet's Metal Working File and municipal questionnaire.

1.1.2.1 **Dunn and Bradstreet Data**

The Dunn and Bradstreet Metal Working File will be geographically reviewed using one of the sorting options available. Primarily, this source will provide information concerning the number and size of metal finishers in thirty candidate areas.

1.1.2.2 Municipal Questionnaire

A municipal questionnaire will be developed and mailed to these thirty locations requesting information from the municipality (such as regulatory constraints, permit assignments, and enforcement procedures) necessary to screen candidate sites according to the criteria developed initially. A cover letter will be mailed with the questionnaire to inform the municipalities selected by the D&B scan of the project's objectives. A telephone survey will be conducted to verify questionable information. Additional, more specific, information may also be collected during this survey of candidate municipalities.

1.1.3 Describe Alternative Regions

A concise report will be prepared for each of the thirty municipalities considered in the selection process highlighting information pertaining to the decision criteria. A summary report will also be prepared to provide an overview of the area surveyed and to include recommendations for the five case study sites. These recommendations will be founded on an analysis of information collected from D&B, the municipal questionnaire, and the telephone survey.

1.2 Develop Decision Tools and Evaluate Five Case Studies

The objective of this section is to develop a computer optimization model to balance the parameters affecting feasibility in each case study. Using these tools, one case study will be chosen for detailed analysis. The model will be user oriented so that it can be easily applied to other situations. The evaluation of the case studies will include recommendations for the demonstration study area. The location chosen will reflect a positive political and technical climate for investigating the feasibility of centralized metal finishing waste treatment.

1.2.1 Develop Industrial Data Base

The information and data necessary to evaluate the case studies will include sources and characteristics of wastes, installed treatment equipment, sludge disposal mechanisms, etc. and will be organized and stored in a data base. Information on participants to be used in the evaluation will be obtained from two major sources:

1. Industrial and business information sources.
2. Industrial questionnaires.

The Dunn and Bradstreet Metal Working File will be used to identify industrial sources and for creating a mailing list for the industrial questionnaire to plants in the candidate studies. The industrial questionnaire will request sources and characteristics of wastes, pollution control and process technology installed, etc. Use of existing EPA data will be included but cannot substitute for the cooperation of industrial people.

1.2.2 Determine Regulatory Constraints

Regulatory constraints will be established by reviewing development documents, Department of Transportation (DOT) regulations, and applicable solid-waste-management guidelines. The investigation will include federal, state, and local elements of regulations and will also concentrate on regional and local mechanisms for issuing permits. Specific problems with the individual studies will be identified. Enabling ordinances will be studied and recommendations made if they do not exist.

1.2.3 Develop and Investigate the Use of Decision Tools for Alternative Areas

The computerized decision tools will be developed and used to optimize on-site vs. off-site treatment to maximize the economic benefits of CWT in the case studies.

1.2.3.1 Develop Decision Tools

The computer model to be used in evaluating CWT will minimize the inversely related functions of transportation and capital operating costs for on-site and centralized treatment using mathematical data and control technology information. Its structure will follow prior work on modeling regional treatment facilities with the added feature of incorporating existing on-site treatment.

1.2.3.2 Develop Scenarios

A series of scenarios for each study, based on the model output, regulatory constraints, and other available information will be produced. These will be introduced into the model for selecting an optimal regional system.

1.2.3.3 Establish Sensitivity of Scenarios

The industrial survey data from the

selected case study sites will be utilized in the model to determine the sensitivity of each scenario to changes in critical variables, such as hauling costs, political constraints, treatment capital and operating expenses to indicate trends where CWT might not be feasible.

1.3 Disseminate Results

Two reports will be developed for Phase I:

1. Capsule report for presenting results on the thirty original candidate regions citing the results of the selection procedure of the five case studies.
2. Project report relating details of the five case studies.

1.3.1 Present Results to Candidates

A capsule report will be issued to the metal finishing industry to summarize the results of the case studies. It will be written in a concise manner and will rely heavily upon graphics to give an indication of CWT feasibility.

1.3.2 Final Report for Phase I

A final engineering report for Phase I will show results of case studies, document project activities, present and summarize data, and describe the analytical model.

PHASE II
DEVELOPMENT OF DETAILED SCHEMATIC FOR DEMONSTRATION OF CENTRALIZED TREATMENT CONCEPT

The objective of Phase II is to develop a comprehensive plan for a centralized waste treatment (CWT) facility for a specific location.

2.1 Develop System Design for Demonstration

There are a number of steps that must be undertaken to design the CWT system properly. These steps include:

1. Determine optimal scheme for CWT components including on-site treatment or concentration of wastes; collection, transportation, treatment and disposal of wastes.
2. Design CWT facility based on current and projected industrial community needs.
3. Determine/develop waste exchange options.
4. Obtain commitments from user companies.
5. Determine technologies for wastewater minimization and on-site treatment and associated costs.

6. Develop and secure financing plan.
7. Develop regional ordinances to permit CWT.
These tasks are discussed as follows.

2.1.1 Determine Optimal Scheme for CWT

To determine the optimal size for the CWT facility and other major system components, various scenarios will be developed through modeling with an optimal CWT scheme forthcoming from the optimization program.

2.1.1.1 Gather and Analyze Data

To supplement and verify the information collected in Phase I, plant surveys will be conducted by visiting all metal-finishing dischargers within the designated area. Prior to the plant visits, completion of a second questionnaire will be requested to provide the detail needed by the model. the detail needed by the model. As plants are visited, the information gathered will be reviewed for validity, entered into the data base, and analyzed. Economic and technical trends will be established. Follow-up telephone calls will be made if information is inadequate or missing.

2.1.1.2 Develop Viable Scenarios

Once all information is entered into the data base, the analytical model will be utilized to compare the options available to the area.

When uncertainty exists, various sets of data will be used to investigate sensitivity. The output of the modeling exercise will be various scenarios each based on valid assumptions. From this set of scenarios, an optimal CWT system will be recommended.

2.1.2 Design Centralized Treatment Facility

The design of the CWT facility will include a detailed design of the treatment systems for various dilute and concentrated wastes and sludge. A segregated landfill will likewise be designed. The individual tasks to be performed in this section are:

- Obtain detailed information on plant influent composition as equalized from each of the participating sources.
- Selection and coordination of various treatment steps (process design).
- Sizing of equipment.

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- Preliminary design of control schemes.
- Development of process flow diagrams and process instrumentation diagrams, equipment specification, and operating philosophy.
- Ultimate disposal philosophy for solid waste.

These design criteria will be provided from modeling results, analysis of regulatory requirements, estimation of raw waste loads, and other available information.

2.1.3 Determine/Develop Waste Exchange Options

Waste exchange options will be investigated based upon waste materials available and raw materials currently purchased for production or treatment processes by the industrial community.

2.1.4 Obtain Commitments from User Companies

A cover letter and form will be mailed to potential user companies that request a nonbinding commitment to use the CWT system. Various options will be indicated on this letter of intent based upon the specifications of the CWT facility. The treatment options will be tendered as services to remove concentrated rinse waters, spent plating baths, precipitated sludge and dewatered sludge from plant sites.

2.1.5 Determine Wastewater Minimization and On-Site Treatment and Associated Costs

Information collected during plant visits will be used to determine needs of potential user companies with respect to waste minimization. A report on waste-minimization techniques that could be applied to potential user companies will be prepared. Costs of treatment will be included in the report.

To disseminate the information to participating companies, a seminar on waste minimization for the benefit of potential user companies may be utilized. Specific applications will be addressed at the seminar.

2.1.6 Develop and Secure Financing Plan

Financing alternatives will be recommended to the region and to the individual participants.

2.2 Publish Results

A comprehensive final report will be prepared which shall include:

1. Project objectives.
1. Methodology
3. Model description (users' manual)
4. Case study results
5. CWT system design
6. Conclusions

PHASE III
DESIGN & CONSTRUCTION
OF CENTRALIZED TREATMENT FACILITY

The objective of Phase III will be to complete all specific plans necessary for facility construction. After it's construction and "shakedown", sufficient monitoring and operating data will be obtained in order to fully evaluate its operation and performance.

3.1 Construction of Facilities
The facilities to be used in the centralized waste treatment scheme will be turnkeyed during this time. This will require that all necessary permits be available prior to construction.

3.2 Acceptance of Facilities
All treatment steps will be tested prior to full acceptance and operation of the plant. Shakedown runs will be completed before the facility is open for full operation.

3.3 Development of Operational and Administrative Data
Once accepted, the facility will be operated for sufficient time to determine any administrative and technical problems. These will be corrected as necessary and recorded on a final report on the facility.

PHASE IV
RETROSPECTIVE ANALYSIS
OF PROGRAM AND DEVELOPMENT PROTOCOL

The protocols developed during the course of this program will be evaluated in terms of their accuracy in predicting economic and administrative feasibility of centralized treatment. The results of the program will be summarized in a capsule report and disseminated through a program report and/or seminars.

Economical Pretreatment — A Job Shop Case History

F. A. Steward and Henry H. Heinz*

The American Plating Company, an electroplating job shop, has been established in Zelienople, Pennsylvania, since 1955. The plant's main business since its inception has been to serve the steel fabricating industry in Southwestern Pennsylvania, and adjacent regions in Ohio and West Virginia. The original facilities included barrel and rack zinc plating, to which a Udylite umbrella-type automatic was later added to handle larger steel structures. The umbrella machine was replaced in 1974 by an in-line programmed hoist machine with $14' \times 3' \times 7'$ deep plating and rinsing modules.

The company considers itself a small job plater with a labor force of approximately 6 - 10 people per shift and an annual billing in the range of $1,000,000. When planning for the installation of the plant, it was recognized that adequate waste treatment facilities would be needed to avoid harmful effects from toxic chemicals, (CN and Cr^{+6}), and metals (Cd, Zn, Cr); also potential corrosive conditions created by the effluent discharged to the local sewage treatment plant. Zelienople is a small community (population 6,000) with, at that time, a sewage treatment plant designed for .2 MGD average daily flow. The discharge from the sewage treatment plant is to a small stream, extensively used for sport fishing. In view of the modest-sized local treatment plant to which the effluent would be discharged, it was thought that the plant effluent should not exceed 10% of the total influent and, therefore, that the waste treatment system should allow significant water conservation.

Description of Plant

As usual with most job plating plants, the original facilities had to be expanded by additions to the plant area. The original building had a floor space area of 10,640 ft.². In 1957 an extension was added to house an automatic rack plater and new boiler. In 1960 a new loading dock and storage area for work in process was added, and in 1972 space was created for an in-line, programmed hoist machine so that the present plant area occupies approximately 27,500 ft.² floor space. Figure 1 shows the floor plan of the plant. Fig. 2 is a plant view.

The only unique feature of the plant design is the floor contour with careful segregation of all sewer inlets from the plant floor area, segregation and collection of all accidental spillage, tank or pump leakage, etc. The cyanide-containing processing tanks are within a curbed

*F. A. Steward, Vice President, Engineering, Lancy
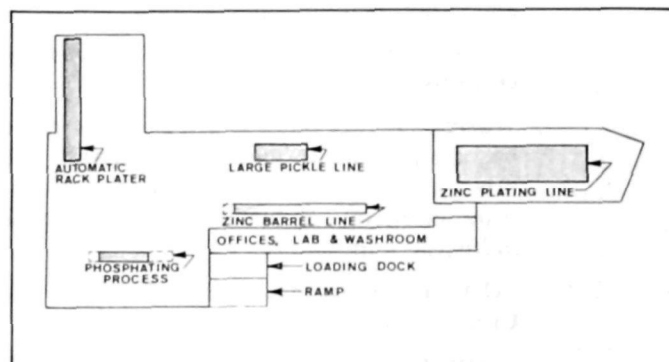Henry H. Heinz, Superintendent, American Plating

Fig. 1—Plant Floor Plan

Fig. 2—View of Plant.

area, channeling any cyanide spill to segregated sumps. Sumps serving the waste treatment system, piping trenches, and pits are all part of the original building and subsequent expansion floor plans, so that the original waste treatment system and improvements could be easily and inexpensively installed and maintained.

Production Equipment and Volume

A. Barrel plating capacity is based on a six-station, 36″ × 14″ barrel, zinc plating line in which originally there was a three-barrel cadmium unit later converted to zinc. Cleaning and pickling occurs in the plating barrels, while rinsing is through an automated hopper line, the work automatically discharged into a gas-heated spiral dryer. The D.C. power is supplied by an 18V, 6000 A rectifier. The average surface area plated in an hour is 250 ft.².

B. The automatic rack machine is an ancient Munning automatic, processing racks 20″ wide, 27″ long, and 6″ deep. Capacity is approximately 100 racks per hour, with a zinc thickness specification of 0.0008″. The D. C. power is 9 V, 15,000 A. The average surface area plated per hour is 360 ft.².

C. The in-line programmed hoist plater has ten plating stations for racks on a crossbar, each accommodating work up to 12' × 5' × 10" deep. The available D.C. power supply is 9 V, 75,000 A. The average surface area handled is 1,584 ft.² per hour. The average zinc plating thickness specification is 0.0008".

D. An overhead bridge crane operated cleaning and pickling line consists of 21' × 4' × 7' deep alkali cleaning, hot sulfuric acid pickling and rinsing tanks. This system is used intermittently for prepickling of hot rolled, rusted, or heavily oiled or flaked hot dip galvanized parts to be plated or stripped; and sometimes also for contract pickling work.

E. A zinc phosphating line under a monorail consists of a phosphating tank 5' × 3' × 3' deep with a rotating barrel, equipped with the usual cleaning, rinsing, oiling, and centrifuging facilities. The line is operated intermittently and has a capacity of 250 ft.² production in an hour.

The company also operates two trailer trucks of 30 ton total payload capacity for the convenience of their customers, picking up and delivering work in the nearby area.

Since August 2, 1978 (from which time this report and cost analysis have been prepared), the plant has been operating two shifts, 21 hours/day, five days per week. Cost data, water consumption and effluent characteristics are all based on this present production volume.

Evaluation of the Waste Treatment Facilities

(a) 1955

The original waste treatment installation at the time of the plant start-up consisted of two Closed-Loop Treatment Rinse (CLTR) systems, one following each cyanide-containing processing step and the other following each chromating process.

Additionally, a waste acid storage tank was installed with the necessary pumping facilities to receive dumped waste acids, cleaners, and accumulating sludges from the treatment rinse systems, treated sludges from the yearly maintenance cleaning of plating tanks, etc. In the Pittsburgh area a number of steel companies are using waste hauling and treatment services on a long-range contract basis. This approach is therefore economical for the plant and avoids the burden of sludge handling and disposal.

It didn't appear necessary to provide a pH control system for the effluent since the cleaners and highly alkaline treatment rinses have maintained a neutral or alkaline pH. The installation of a settling tank for the final effluent didn't appear necessary either. The CLTR systems capture the metals in the dragout.

The effluent flow volume at this time was in the range of 15-20 GPM and has met the stipulated requirements of the consultants of the local sewage treatment plant.

The agreed-upon limits were as shown in Table I.

With the installation of the rack automatic plater and the umbrella automatic, the effluent flow volume increased to 40-50 GPM. The zinc, cadmium, and iron levels in the effluent increased to the point that the company was found to be in violation of the mass discharge limits that were stipulated. Although the sewage treatment plant capacity was also more than doubled (.5 MGD), the consultants of the sewage treatment plant felt that safeguards were needed against potential pass-through of iron cyanides into the stream stocked with fish. Therefore the cyanide limits were changed to also include iron cyanides.

The new maximum level of discharge for CN was now 0.035 lbs./hour, but included iron cyanides. Calculating the stipulated maximum allowable residuals with an effluent flow rate of 50 GPM, it was found that the pollutant concentrations would have to be maintained below the levels shown in Table II.

The iron cyanides in the zinc plating solutions were high and couldn't be easily reduced with chlorination; the cooling water requirements, in view of the high current density plating systems, continued to increase; and the costs for water and sewer rental were continually increasing. Therefore, it was decided to install additional facilities to meet the future requirements. Two systems were added:

(1) An additional CLTR system for neutralization of acid and alkali treatment processes; and

(2) A recirculating cooling water system.

The neutralizing treatment rinse was used after cleaners, acids, phosphating, and after the cyanide treatment rinses. It provided effective chemical rinsing so that a total water consumption and discharge of 12-15 GPM) flow rate, we have 454:57 = 7.57 as a multiplying factor to be used for the conversion of concentration trouble-free compliance with the agreed-upon limits for the residuals.

TABLE I MASS DISCHARGE LEVELS OF POLLUTIONAL PARAMETERS	
Cyanide (exclusing iron cyanide)	0.028 lb./hour
Cyanates (CNO)	0.15 lb./hour
Zinc (Zn)	0.224 lb./hour
Chromium (trivalent) (Cr^{+3})	0.224 lb./hour
Chromium (hexavalent) (Cr^{+6})	0.056 lb./hour
Cadmium (Cd)	0.224 lb./hour
Iron (Fe)	0.55 lb./hour

TABLE II CALCULATED RESIDUALS BASED ON 50 GPM EFFLUENT FLOW	
CN (total)	1.1 mg l
CNO	4.9 mg l
Zn (total)	8.9 mg l
Cr^{+3}	8.9 mg l
Cr^{+6}	1.8 mg l
Cd (total)	8.9 mg l
Fe (total)	18 mg l

A cooling tower was installed to allow recirculation of the cooling waters. The cooling tower discharges to a reservoir tank from where the water is recirculated back to the heat exchangers and serves also the rinse tanks. Rinse water provides the blowdown for the recirculated cooling water. Fresh water is added to the cooling water reservoir to make up for the rinse water consumption. To guard against possible undetected cyanide leaks from the heat exchangers into the cooling water, a cyanide monitor/controller with hypochlorite feed and alarm has also been installed.

The New EPA Pretreatment Regulations

In February, EPA published Proposed Pretreatment Standards for the Electroplating Category. In the interim, a large regional sewage treatment plant was being built which would take over the sanitary waste treatment responsibilities from, among others, the Zelienople treatment plant. The Authority of the regional plant and their consultants do not feel bound by the agreement regarding the allowable residuals that have been in force for the last 22 years, but expect American Plating to meet the proposed EPA guidelines by the time the new regional system begins operation, at year-end 1978. The guidelines proposed in February, 1978, do not mention the applicable mass discharge limits. It is evident that a plant which through the years has followed a design concept of aiming for improved waste treatment by chemical rinsing or other water conservation practices would be at a serious disadvantage if mass discharge limits could not be considered. EPA's General Pretreatment Standards (Fed. Reg. 6/28/78) correct this omission, and indicate that the final pretreatment regulation for each industrial category, although written with concentration limits, will provide equivalent mass limits so that the local or state regulatory agency may use these instead of the concentration limits.

EPA's Guidelines Division has not yet decided what the calculation factors will be, but believes the mass limits will be based on surface area processed and the number of operations, similar to the approach used for the proposed Electroplating Direct Discharge Regulations published in April, 1975. These have been set aside, awaiting reappraisal. Therefore, our calculations have to be based on assumptions. For example, we feel strongly that cleaning and pickling should each be accepted as an "operation," but we calculated on the basis of only two operations—plating and chromating. Similarly, not knowing what water consumption rate will be eventually assumed, we have calculated the anticipated EPA requirements on the basis of 80 l/m²-operation. To be conservative, we have also assumed that in view of job plating practices, it would be safer to consider only two of the five processing lines in operation at any one time. Thus, we have taken the automatic hoist line (1,584 ft.²/hour) and barrel line (250 ft.²/hour) to give a total production rate of 1,834 ft.²/hour.

Our calculations therefore show:

$$1,834 \text{ ft.}^2/\text{hour} = 2.84 \text{ m}^2/\text{min.}$$
2.84 m²/min. × 2 operations × 80 liters/m²-operation = 454.3 l/min.

Dividing 454.3 l/min. by the actual flow rate gives us a multiplier factor to apply against the concentration limits of each parameter as given in the EPA Proposed Guidelines for Pretreatment for the Electroplating Category. Assuming 57 l/minute (approximately 15 GPM) flow rate, we have 454:60 = 7.57 as a multiplying factor to be used for the conversion of concentration limits to be on a mass discharge basis.

Table III shows the calculated allowable residuals:

Comparing these allowable residuals with the results of routine analytical analyses, as shown in Table IV, shows that the plant is safely below the anticipated federal requirements.

Current Plans - A Further Improvement

Recognizing that the discharge rate is so close to the 10,000 gallons/day definition for a small plant makes a further reduction in water usage appear attractive.

TABLE III
CONVERSION OF EPA'S CONCENTRATION LIMITS BASED ON ALLOWABLE MASS DISCHARGE

	Zelienople Limits at 15 GPM	Feb., 1978 EPA Max./Day	30 Day Ave.
CN^	included in CN₁	1.5 mg l	0.6 mg l
CN'	3.8 mg/l	4.8	1.8
Cr⁺	6.1	1.9	0.7
Cr'	30.3	31.8	12.1
Zn'	24.2	25.7	11.3
Total Metals		56.8	29.5

TABLE IV
TABULATED ANALYTICAL RESULTS
(mg/l)

	8/30/78	9/7/78	9/14/78	10/10/78	10/20/78	11/30/78
CN^	0.43	<0.01	0.02	<0.01	<0.01	0.01
CN'	0.43	0.22	0.02	0.55	<0.01	0.01
Cr⁺	<0.01	<0.01	<0.01	<0.01	<0.01	0.26
Cr'	<0.01	<0.01	<0.01	0.03	<0.01	0.49
ZN'	4.65	4.85	1.52	4.30	3.20	7.60
Total Metals	5.27	5.92	2.38	6.37	3.52	11.29
pH	10.4	9.85	9.75	10.5	10.3	7.8

Achieving classification as a small plant would allow a reduction in analysis and monitoring costs for both the plant and Regional Authority for zinc, iron, total chromium, etc. The proposed EPA regulations didn't spell out whether the 10,000 gallons/day applies to an 8-hour working day or a 24-hour calendar day. Because the plant had to meet the Regional Sewage Authority deadline before the end of the year, and because the actual manner for the calculation of mass discharge limits is not officially available, further steps are being taken on the conservative assumption that EPA meant 10,000 gal./calendar day. After tightening up all unneccessary water usage in the plant, it is believed that with the addition of a better steam condensate return system, the discharged process wastes will be safely within the 10,000 GPD small plant category. Table V shows the daily water consumption volume and the manner this has been reduced since August 1 when this program started. The 10,000 GPD reflects on all the water used in the plant, including sanitary consumption. (10,000 GPD converted for 21-hour operation indicates 7.9 GPM total water usage).

The new equipment that has been ordered but not yet installed consists of a condensate collection and pumping system, including conductivity monitoring and alarm. The anticipated savings amount to approximately 3,000-3,500 GPD of high-quality hot water. This installation will save in water, boiler treatment chemicals, and heating energy. The system should pay for itself within six months.

Under these conditions, according to the February, 1978, proposed EPA standards for plants discharging less than 10,000 GPD process waste, the effluent requirements for the plant would be limited to the parameters shown in Table VI.

Based on the routine analyses, as have been shown in Table IV, the EPA requirements can be met without any changes in the waste treatment system.

Zinc Plating Process Sequence

A brief explanation of the Closed-Loop Treatment Rinse approach and the processing sequence will illustrate how such unusually low water consumption can be achieved.

The CLTR concept employs chemical rinses to remove the dragout film from the metal surface emerging from a processing solution. The chemical rinse is so formulated that an excess of treatment chemicals is available to eliminate the particular harmful content in the dragout. The chemical to be treated may be cyanide, hexavalent chromium, metals to be precipitated, or just acidity or alkalinity to be neutralized. The treatment solution is recirculated from rinse tanks in the processing lines to a reservoir which serves also as a settling tank for the precipitates. Chemical depletion due to reactions with the dragout is replenished by chemical additions, most often through an automatic controller. The final rinse waters or fresh water additions at a low flow rate create a blow-down for each system so that the total dissolved salt concentration is held constant.

TABLE V
DAILY EFFLUENT VOLUME

Date	Operating Hrs.	GPD
8 30 78	17	14860
9 7 78	17	9120
9 14 78	17	8050
10 10 78	17	7300
10 20 78	17	4310
11 30 78	17	3980

TABLE VI
EFFLUENT LIMITS FOR PLANTS DISCHARGING LESS THAN 10,000 GPD PROCESS WASTE

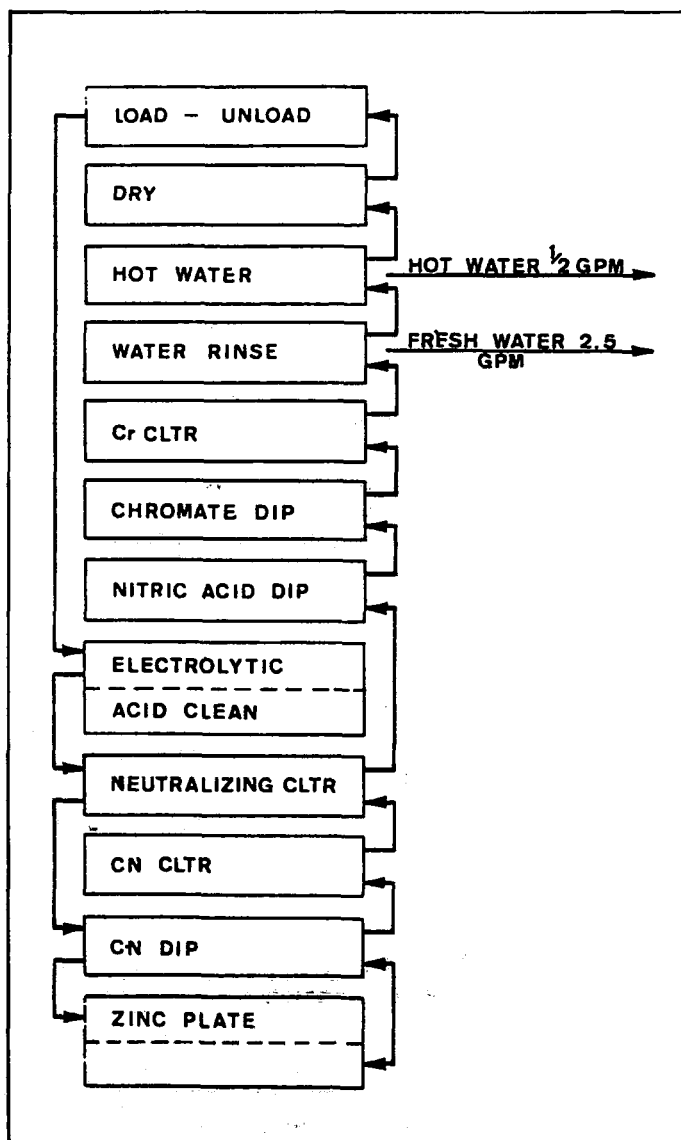|	Max./day	30 Day Ave.
CN^A	2 mg/l	0.8 mg/l
Cr	0.25	0.09

Fig. 3—Process Sequence.

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In the American Plating installation, as described earlier, three CLTR systems are used. The "Cyanide Treatment" is an alkaline solution containing 1,500-1,800 mg/l chlorine; the "Chromium Treatment" is an alkaline solution containing 300-500 mg l hydrazine as a reducer; the "Neutralize Rinse" is a slightly alkaline solution maintained by caustic soda or sulfuric acid additions.

To illustrate the processing sequence and fresh water usage, Figure 3 is a schematic view of the automatic hoist process line.

As can be seen from Figure 3, throughout the processing cycle, chemical rinsing is employed and fresh water is used only for final rinsing and the hot water rinse. The concept is not new; many installations designed and supplied by Lancy achieve even greater water conservation by recycling the final rinses through an ion exchange system.

Probably unique to this plant is the extensive use of electrolytic acid cleaners. These not only save a process and rinse step, and thereby reduce chemical loading on the waste treatment system, but they also shorten the plating line, saving space and time for the automatic hoists.

Waste Treatment Equipment and Installation Cost

It is nearly impossible to reconstruct accurately the equipment and installation costs because the major part of the installation was paid for with 1954 and 1960 dollars; the installation was done by plant personnel; and all costs have been amortized a long time ago. Checking old records and reconstructing the events, a conservative estimate is as follows:

1954   Two Integrated Treatment System reservoir and sump tanks, level controllers, pumps, hypochlorite solution, and waste acid storage tanks, installation, piping, wiring, etc. .... $12,000.

1960   Integrated Neutralize System Reservoir, sump tanks, level controllers, pumps, stock solution tanks for caustic soda, sulfuric acid, pH controller .... 14,000.

Cooling water monitor cyanide and controller installed .... 3,000.

1978   Estimated: Condensate return collecting system with pumps, monitor, and controller, installed .... 5,000.

Total Capital Cost .... $34,000.

Note: This excludes the cooling water system which is considered process equipment.

Waste Treatment Operating and Maintenance Costs and Savings

A. Total Costs:

a. Acid and sludge disposal - 4,500 gal./load,
   8 loads/month @ $0.10/gallon $3,600

b. Chemicals:

Hypochlorite - 2,675 gal. @ $.55/gal.	$1,471.25
Caustic Soda - 5,750 lbs. @ $0.16/lb.	955.08
Sulfuric Acid - 576 gal. @ $0.46/gal.	264.96
Hydrazine - 270 lbs. @ $2.00/lb.	540.00
Soda Ash - 120 lbs. @ $.05/lb.	6.00
Total Chemical Cost	**$3,237.29**

c. Labor:
   Foremen (2) - waste treatment checks -
   ½ hr./shift = 20 hrs/mo.
   Foreman (1) - daily spot checks -
   ½ hr./day = 10 hrs/mo.
   @ $10.01/hour   300.30
   Operating Labor (2) - chemicals make-up,
   checking, 15 min./shift =
   20 hrs./mo. @ $5.42/hour =   108.40

   Total Labor Cost   408.70

d. Maintenance
   Labor, maintenance men (2) -
   5 hrs./week ea.
   @ $6.43/hour   257.20
   Material, spare parts/mo.   300.00

   Total Maintenance   557.20

e. Outside laboratory analysis services,
   once per month   100.00

   Total Operating Costs, Waste Treatment $7,903.19/mo.

B. Savings Through Reduced Water Consumption:

Present water charges are $0.674/M gallons; the sewer rental cost is $0.575/M gallons for a total of 1.249/M gallons.

Using the EPA minimal water usage formula of 80 l/m^2-operation × 2 operations × the surface area processed, which in this case is 2.84 m^2/minute (two process lines in operation), as calculated before, gives 454.3 l/minute as a flow volume.

This flow rate gives a daily (21 hr.) water usage factor of 150,636 gallons. Taking, as before, 20 working days, month, and the combined water and waste water cost of $1.249/M gallons, it may be conservatively projected that without water conservation in waste treatment, the cost would be $3,762.89

The present water usage is less than 10,000 GPD (21 hrs.) (includes sanitary usage also); for a 20-day month, this is

                  249.80

This amounts to a saving of $3,513.09

C. Net Costs:

Deducting the savings from the total costs of $7,903.19, the actual monthly operating and maintenance cost is $4,390.01.

Considering the average plant operating costs, which are $85,000/month, it appears that the waste treatment cost is 5.16% of the operating cost.

City of Grand Rapids, Michigan Program of Industrial Waste Control

James A. Biener*

Introduction

Over the past nine years, the City of Grand Rapids has experienced the differential effects of both non-control of industrial pollutants and tight regulation of industry's use of sanitary sewer system. This paper is presented in order to share the experiences of Grand Rapids in the area of water pollution control and the methods developed to attain and maintain high water quality standards.

The City of Grand Rapids is the largest city in Michigan's western lower peninsula with a population of 190,000 within the City limits and 350,000 in the metropolitan area. The Grand River is in the heart of Grand Rapids and is an important recreational resource for western Michigan. Industry is highly diversified in the metropolitan area, although Grand Rapids is perhaps best known for its production of fine furniture. One of the largest concentrations of electroplating firms in the country exists in this area, with over 35 companies engaged in this automotive-related activity.

During the late 1950's and 1960's industrial contamination of the Grand River created severe environmental problems. Periodic fish kills were caused by high discharges of cyanide and heavy metals from the metal plating industry in the area.

As the environmental movement gained momentum during the mid-1960's, public attention in Grand Rapids was focused on the deteriorating state of the once healthy Grand River. The time for reversing the damaging trend then arrived in Grand Rapids. In January of 1969 the Grand Rapids City Commission enacted a comprehensive Water Pollution Control (now called Sewer Use) Ordinance, establishing effluent limitations for cyanide and heavy metals, as well as other provisions. Considerable effort was required to reach this point, however. Metal platers in the area lobbied strenuously against any limitations, arguing that the cost of pretreatment of wastes would force them to relocate elsewhere. City policymakers were forced to deal with those issues and acknowledge that comparable effluent standards did not exist elsewhere in the state. Nevertheless, concern for the quality of the water and the

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general environment remained the focus, and the Ordinance was adopted as City law.

Water pollution control is the responsibility of the City Wastewater Treatment Plant, a division of the Environmental Protection Department. In addition to serving the City's wastewater disposal needs, the Grand Rapids plant provides service to eleven cities and townships on a contractual basis. The capacity of the activated sludge wastewater treatment plant is currently being expanded from 45 MGD to 90 MGD, with assistance of an E.P.A. construction grant. Sludge digestion is being phased out in the new design and being replaced by a new heat treatment process. With this new process, sludge incineration will be the principal means of sludge disposal.

The Sewer Use Ordinance and Industrial Sewer Use Regulations currently in effect were adopted in substantially the same form in 1969. They set forth the standards, rules and regulations with which industrial users of the sewer system must comply, as well as provisions for enforcement and management of the law.

Sewer Use Ordinance

"2.63. Management of the Sewage Disposal System. The Grand Rapids Sewage Disposal System shall be and remain under the management, supervision, and control of the City Manager who may employ or designate such person or persons in such capacity or capacities as he deems advisable to carry out the efficient management and operation of the System. The City Manager or his designee may make such rules, orders or regulations as he deems advisable and necessary to assure the efficient management and operation of the System; subject, however, to the rights, powers and duties with respect thereto which are reserved by law to the City Commission of Grand Rapids.

"2.64. Standards, Rules and Regulations. The standards, rules and regulations established in or pursuant to this chapter are deemed to be the absolute minimum consistent with the preservation of the public health, safety and welfare, to prevent pollution of the environment, and to fulfill the obligations of the City with respect to State and Federal law and all rules and regulations adopted in conformance thereto. The discharge into the System of any substance which exceeds the limitations contained herein, or in any manner fails to conform hereto, is hereby declared to be a public nuisance, and a violation of this Code.

"2.65. Use of the Sewage Disposal System. Any person conforming to the standards, rules and regulations established in or pursuant to this chapter shall be permitted to discharge effluent into the System provided there exists adequate sewer service available to which he can connect.

"2.66. Prohibites Substances. Except as hereinafter provided no person shall discharge or cause to be discharged any of the following substances into the sanitary or combined sewer:

(1) Any effluent having a temperature higher than 140 degrees F.

(2) Any effluent which contains more than 50 mg/l of animal fat, vegetable fat, oil or grease, or any combination thereof.

(3) Any gasoline, benzene, naphtha, fuel oil or other inflammable or explosive liquid, solid or gas.

(4) Any grease, oil or other substance that will become solid or viscous at temperatures 60 degrees Celsius and below after entering the System.

(5) Any substance from the preparation, cooking and dispensing of food and from the handling, storage and sale of produce which has not been shredded to such a degree that all particles shall be carried freely under flow conditions normally prevailing in the public sanitary or combined sewer, with no particle larger than one-half inch in any dimension.

(6) Any substance capable of causing obstruction to the flow in sewers or other interference with the proper operation of the sewage disposal system including but not limited to mineral oil, grease, ashes, cinders, sand, mud, plastics, wood, paunch manure, straw, shavings, metal, glass, rags, feathers, asphalt, tar and manure.

(7) Any effluent pH lower than 6.0 or higher than 10.0 or having any other corrosive properties capable of causing damage or hazard to structures, equipment or personnel of the the treatment works.

(8) (a) Any effluent in excess of:

1.5 mg/l of Cadmium as Cd.
6 mg/l of Zinc as Zn.
2 mg/l of total Chromium as Cr.
1.5 mg/l of Copper as Cu.
1 mg/l of Cyanide as CN.
1.5 mg/l of Nickel as Ni.
.02 mg/l of Phenol or derivative of Phenol.

(b) Any discharge of phosphorus, ammonia, nitrates, sugars or other nutrients or waste waters containing them which have an adverse effect on treatment processes or cause stimulation of growths of algae, weeds, and slimes which are or may become injurious to water supply, recreational use of water, fish, wildlife, and other acquatic life.

(9) Any paints, oils, lacquers, thinners or solvents including any waste containing a toxic or deleterious substances which impair the Sewage Treatment process or constitute a hazard to employees working in the Sewage Disposal System.

(10) Any noxious or malodorous gas or substance capable of creating a public nuisance.

(11) Any effluent of such character or quantity that unusual attention or expense is required to handle such materials at the sewage treatment plant or to maintain the System.

(12) Any discoloration such as, but not limited to, dyes, inks, and vegetable tanning solutions, or any unusual chemical oxygen demand, chlorides, sulfates or chlorine requirements in such quantities as to be deleterious and a hazard to the System and its employees.

(13) Any radioactive wastes or isotopes of such half-life or concentration as may exceed limits established by applicable Local, State or Federal regulations.

(14) Any effluent containing a five (5) day biochemical oxygen demand greater than 300 mg/l.

(15) Any effluent containing suspended solids greater than 350 mg/l.

(16) Any effluent containing phosphorus greater than 40 mg/l.

(17) Any effluent having an average daily flow greater than 2% of the System's average daily flow.

The Director upon review may approve discharges in excess of the limits set forth in subsections 14 through 17 subject to conditions either set forth in this chapter or special conditions he deems necessary in order to preserve and protect public health, safety and welfare, subject to conformance with the applicable State and Federal law.

"2.67. Inspection. The Director and other duly authorized employees of the City bearing proper credentials and identification shall be permitted to enter upon all properties at reasonable times for the purpose of inspection, observation, measurement, sampling and testing in accordance with the provisions of this chapter and any rules and regulations adopted pursuant hereto. Any person who applies for and/or receives services from this System under this chapter shall be deemed to have consented to inspections pursuant to this section, including entrance upon that person's property at reasonable times to make inspections.

"2.68. Use of Storm Sewers. No person shall discharge or cause to be discharged into any storm sewer or natural or artificial water course, effluent other than strom water or uncontaminated effluent, except with authorization by a National Pollution Discharge Elimination System permit, and with the approval of the City's Director of Environmental Protection.

"2.69. Protection from Damage. No unauthorized person shall maliciously, willfully or negligently break, damage, destroy, uncover, deface or tamper with or alter any structure, property, appurtenance, equipment or any other item which is part of the Sewage Disposal System.

"2.70. Enforcement. Any person found to be violating any of the provisions of this chapter shall be guilty of a violation of the Code. The Director is hereby authorized to bring any appropriate action in the name of the City of Grand Rapids, as may be necessary or desirable to restrain or enjoin any public nuisance, to

enforce any of the provisions of this chapter, to initiate criminal prosecution, and in general to carry out the intent and purpose of this chapter."

Industrial Sewer Use Regulations

R-1. Industrial Cost Recovery System - All industrial users, connected to the Grand Rapids Sewage Disposal System, shall be required to pay their share of existing EPA grants and any grant or grants awarded pursuant thereto, divided by the recovery period. All industrial users shall share proportionately, based on flow, in the recovered amounts. Industrial users shall also pay a surcharge on Biochemical Oxygen Demand (BOD) and Suspended Solids (SS) on individual plant effluents in excess of 300 mg/l of BOD and 350 mg/l of SS.

R-2. Inspection - When required by the Director, the owner or occupant of any property served by a sewer carrying industrial or commercial waste shall install one or more suitable control manholes to facilitate observation, sampling and measurement of discharges. Such manholes when required shall be accessible and safely located and shall be constructed in accordance with plans approved by the Director. The manholes shall be installed by the owner at his expense and shall be maintained by him so to be safe and accessible at all times, in the event that no manhole has been required, the Director shall designate a proper sampling point.

R-3. Testing Method - All measurements, tests, and analyses of the characteristics of discharges shall be determined in accordance with standard methods, herein defined, and shall be determined by taking suitable samples at designated sampling points. Such sampling shall be an appropriate manner of determining both compliance with the requirements and penalties specified in the Ordinance.

The City and all users of the Sewage Disposal System shall employ one of the following standard methods for the analysis of effluent:
   a. **Standard Methods for the Examination of Water and Wastewater,** available from the American Public Health Association;
   b. **American Society for Testing and Materials (ASTM) Annual Book of Standards, Part 31;** or
   c. **Environmental Protection Agency Methods for Chemical Analysis of Water and Wastes.**

Users shall maintain a sampling frequency which insures that Ordinance limitations for effluent are met.

R-4. Industrial Surveillance Program - The City shall sample industrial effluent entering the Sewage Disposal System. One of two methods of industrial surveillance shall be utilized for each industry:
   a. For those industries contributing toxic or deleterious substances regulated and controlled by the City Sewer Use Ordinance, the following procedure shall be followed: A grab sample shall be taken at the designated sampling point.
   b. For those industries contributing non-toxic wastes exceeding amounts specified by the City Sewer Use Ordinance, the following procedure shall be followed: Three twenty-four (24) hour composite samples shall be taken at the designated sampling point during each quarterly billing period.

Tests on all industrial surveillance samples shall be performed in accordance with **Standard Methods for the examination of Water and Wastewater.**

R-5. Penalty Charge Methods (Surcharge) - All users of the Sewage Disposal System shall be subject to penalty charges for effluent containing Biochemical Oxygen Demand (BOD) in excess of 300 milligrams per liter, and Suspended Solids (SS) in excess of 350 milligrams per liter. The City shall collect three (3) twenty-four (24) hour composite samples from each designated sampling point once each billing period, and base the surcharge cost upon such samples. The penalty charge shall be calculated by an employee designated by the Director and billed quarterly by the Water Department.

R-6. Preliminary Treatment Facilities - Where necessary, in the opinion of the Director, the owner shall provide at his expense, such preliminary treatment as may be necessary to:
   a. Reduce the biochemical oxygen demand to 300 mg/l and the suspended solids to 350 mg/l, or
   b. Control toxic or deleterious substances, or
   c. Control of the quantities and rates of discharge of such water and wastes.

Plans and specifications and any other pertinent information relating to proposed preliminary treatment facilities shall be submitted for review by the Director. No construction of such facilities shall be commenced until the review has been completed.

Where preliminary treatment facilities are provided for any discharges, they shall be maintained continuously in satisfactory and effective operation, by the owner at his expense. Any person required to utilize preliminary treatment facilities shall, upon the request of the Director, submit to the Director, records of samplings taken from waste discharges.

R-7. Septic Tank Waste - Disposal of Sludge from Pretreatment Systems - Sludge from an industrial

or commercial pretreatment system shall not be placed into the Sewage Disposal System. Such sludge shall be disposed of by a licensed hauler in a site approved by the Michigan Department of Natural Resources.

Sections 2.63 and 2.70 designate the management authority and legal authority necessary to implement and enforce the Ordinance and the Regulations. Sections 2.64 and 2.65 subject all users to the provisions of the Ordinance and the Regulations designate violations as a public nuisance subject to penalty. Section 2.67 permits inspection of the customers' premises by properly authorized employees.

R-2 provides the authority to require the construction of a sampling manhole if required. R-3 designates the standard methods that are to be used for effluent analysis. R-4 designates a grab sample as an acceptable sampling procedure for toxic wastes. R-6 designates the responsibility for construction, operation and maintenance of pretreatment facilities. R-8 requires that all residue sludges be disposed of in a properly licensed site.

Initial Enforcement Program

The effluent limitations stipulated in the Sewer Use Ordinance and accompanying Regulations required significant changes in industrial waste disposal practices. Local industry was required to invest several million dollars into the design and construction of effluent pretreatment facilities and had to provide the funds to sustain the daily operation.

At the time of enactment of the Ordinance, the City recognized that compliance with the limitations would be best achieved through cooperation between the City and local industry. The initial step taken by the City was to attempt to improve its already strained relationship with industry through personal contact with representatives of affected companies in the area, and through providing short-term variances to those companies.

Each company was granted a two-year variance to the Ordinance which allowed them to exceed effluent limitations, provided that the City could determine that satisfactory progress was being made toward construction of a pretreatment facility. The variance stipulated that industry must file a set of design plans with the City for its pretreatment system within six (6) months and submit progress reports every six (6) months thereafter.

During the first six months of the program, City staff visited each of the companies to meet management personnel and to explain the details of the effluent limitations. It was explained that the City staff would be responsible to monitor the industrial waste on a continuous basis and to recommend whatever legal action was necessary to achieve compliance. The industry was informed that we would share samples and compare analyses at their request. The City's role was represented as that of a "helpful guardian" of their effluent.

During the variance period it was recognized that the effluent limitations were not achievable within the two (2) year period and that the variance had to be extended for six (6) months. Although industry had in most cases made a good faith effort to meet the deadline, delivery of pumps, motors and other electrical equipment was slower than anticipated and was not received in time to complete the pretreatment system in every plant. The six (6) month extension was offered as a "shake down" period after which active enforcement would begin.

Compliance Procedures

Following the two and one-half year variance period, industries were subject to penalties for effluent limitation violations. A standard procedure, outlined below, was adopted by the City to assure uniform treatment for all violations. While the procedure was developed with a view towards achieving voluntary compliance, powers of prosecution were specified to insure compliance.

1. The person responsible for a particular industry's pretreatment system is formally notified of any violation and directed to take immediate corrective action. If such action is taken and is effective in abating the violation, the City takes no further action.
2. If any effluent limitations continue to be violated, a complaint is filed by the City Attorney's office and a warrant is issued by the court against the company.
3. After a warrant is issued and prior to scheduling a trial, the company's officials and attorney are invited to a pre-trial hearing to discuss the company's violation and actions. If this meeting results in commitments by the company to specific corrective measures, the warrant is held in abeyance until such time that effluent sampling by City staff indicates compliance with the limitations. When compliance is achieved, the warrant is often cancelled.
4. If the company continues to violate the effluent standards the warrant is sent to the court in order for a trial to be scheduled. The company may enter a plea up to the time of the trial.

In most cases, court trials result in convictions and fines. Company fines usually consist of the maximum City code penalty of $100 per violation, City costs of surveillance and court costs. The heaviest fine levied against a single industry was almost $5,000, representing 41 violations of the Ordinance plus City surveillance costs. The court authorized payment directly to the Environmental Protection Department for the surveillance expensed involved.

A total of 212 warrants have been issued for effluent limitation violations since 1971. Of this number approximately twenty-five (25) percent have gone to trial. The majority of the warrants have been resolved in pre-trial conferences.

Collection & Disposal of Industrial Sludges

Effective control of industrial waste requires proper collection and disposal of the residual materials resulting

from pretreatment systems of industries. Sizable quantities of both liquid and solid metallic hydroxide sludge began to be generated in the Grand Rapids area once the pretreatment systems became operable. The liquid sludges were 2 - 6% solids and were generated by those companies that had no physical space for dewatering equipment or felt that liquid disposal was more economical for them. Other companies installed vacuum filters, centrifuges or other filtering devices to solidify their sludges to solid contents of 20 - 30% with the consistency of conventional vacuum filtered sewage sludges.

Creation of industrial sludges created a local demand for transportation and disposal of these wastes. One local company suddenly developed · into a rather major operation with the purchase of several large tandem trucks for the transportation of the liquid sludges. Another company bought some tank trucks for liquid waste and supplied other containerized equipment for transporting the solid wastes. This same company constructed sand bed dewatering cells for dewatering the liquid sludges before transporting to a disposal site.

Disposal of both the liquid and solid metallic hydroxide sludges were under the jurisdiction of the Michigan Department of Natural Resources. Little attention was paid to the disposal practices, as no specified State legislation applied and no previous experience existed. Disposal sites were approved quite readily by the DNR. During the first five or six years of the industrial program, solid sludges were co-disposed with solid waste in sanitary landfills or placed in an approved site in an abandoned gravel pit. Liquid sludges were dewatered in the sand bed filters of a private hauler, or applied directly on the land at the gravel pit site.

Recently, monitoring wells located near the gravel pit site showed a migration of heavy metals into the water table. The site has been closed for disposal of metal hydroxide sludges and State legislation has been enacted to establish standards for land disposal of industrial sludges. Co-disposal of liquid or solid metallic hydroxide with general refuse is not allowed. Separate sites for disposal of industrial wastes are required, and the standards for these sites dictate sufficient clay thicknesses that prevent any migration in either a vertical or horizontal direction.

The present Michigan standards for industrial waste disposal sites are very restrictive and can only be met when the area being considered has clay depths of 25 to 30 feet. The process of evaluating an industrial disposal site involves public hearing procedures which always result in negative public reaction that prevents the development of a site or at least delays the development. The process required to license an industrial site is equal to or more complicated than obtaining a license for a sanitary landfill operation.
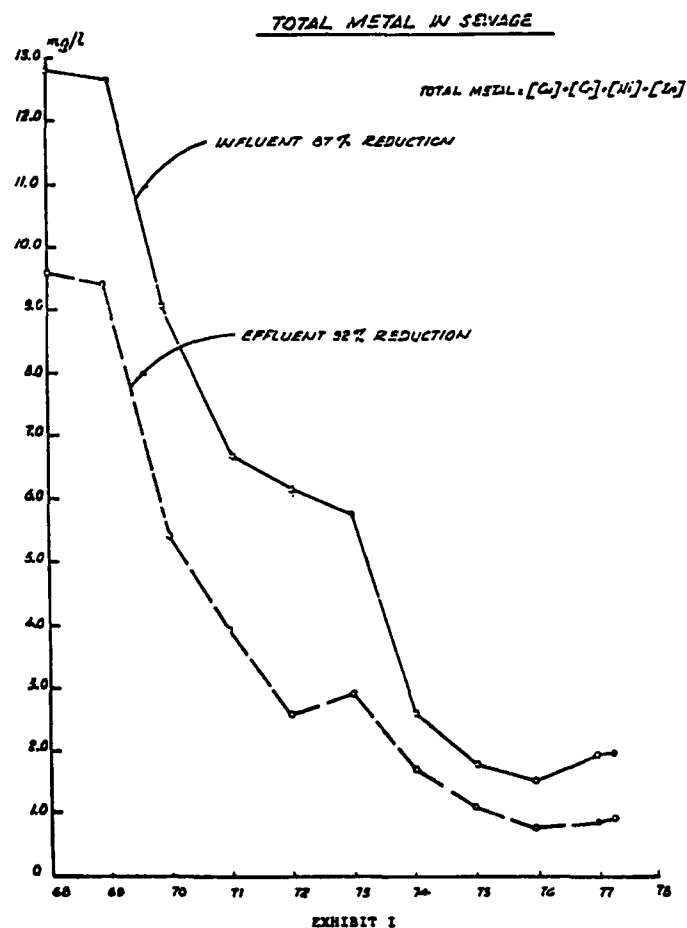
At the present time, there is no licensed site in or near Grand Rapids for the disposal of either liquid or solid sludges. Many companies are contracting to have their waste hauled long distances for disposal and in most cases to the State of Illinois or Indiana. A temporary storage site for solid sludges has recently been approved although the sludge must be removed from this site to a permanent site for final disposal. The cost for transporting and disposing of sludge has tripled or quadrupled in the past six months because of the lack of a local disposal site.
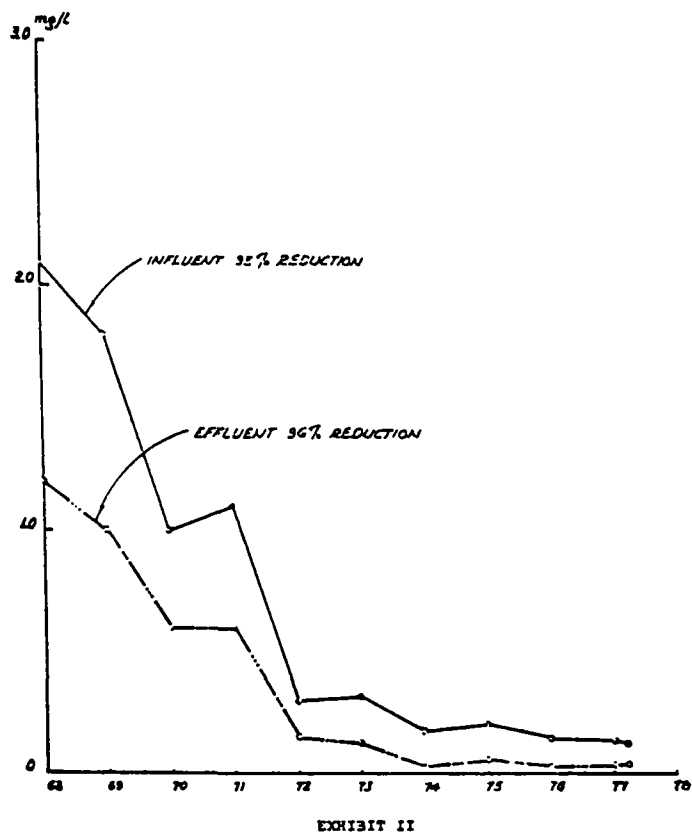
The present sludge disposal dilemma is not near an end. A local site meets all the criteria of the State licensing regulations but is being blocked by public reaction and pressure in the township where it is proposed. Pressure has also begun to develop from the other states where the sludges are being deposited. We can only hope that a disposal site or sites are developed before industry has no choice but to dispose of its waste into the public sewer, and we are once again back where we started in 1969.
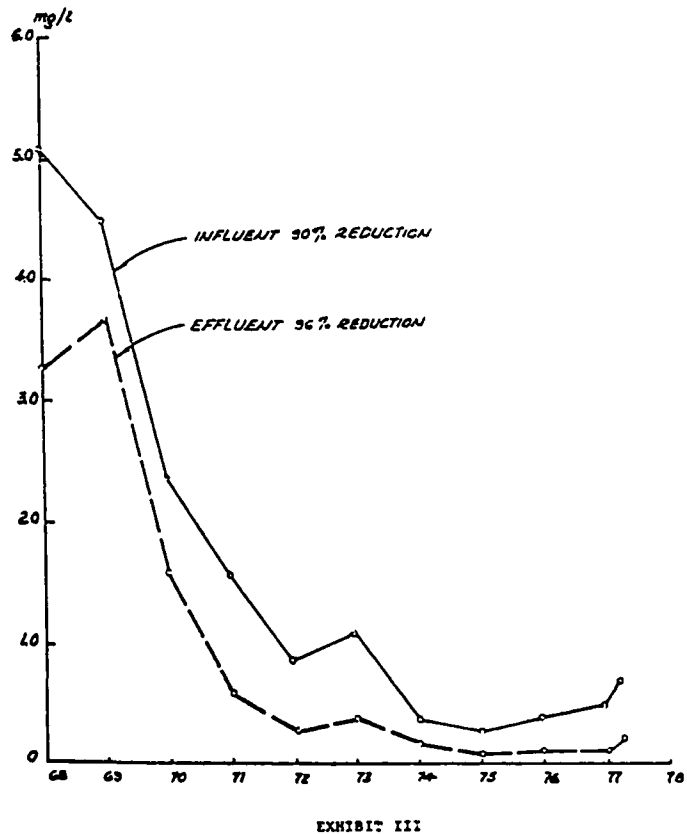
Effects of Pretreatment Ordinance

Since adoption of the pretreatment Ordinance, there have been significant reductions in metal concentrations found in sewage influent and effluent. Total metal concentration in Grand Rapids sewage is shown in Exhibit I. Influent levels have dropped from the 12-13 mg/l range to about 2 mg/l. Effluent levels have dropped from the 9-10 mg/l range to close to 1 mg/l (representing 87% and 92% reduction respectively). Exhibit II shows that a similar experience with total cyanide concentration
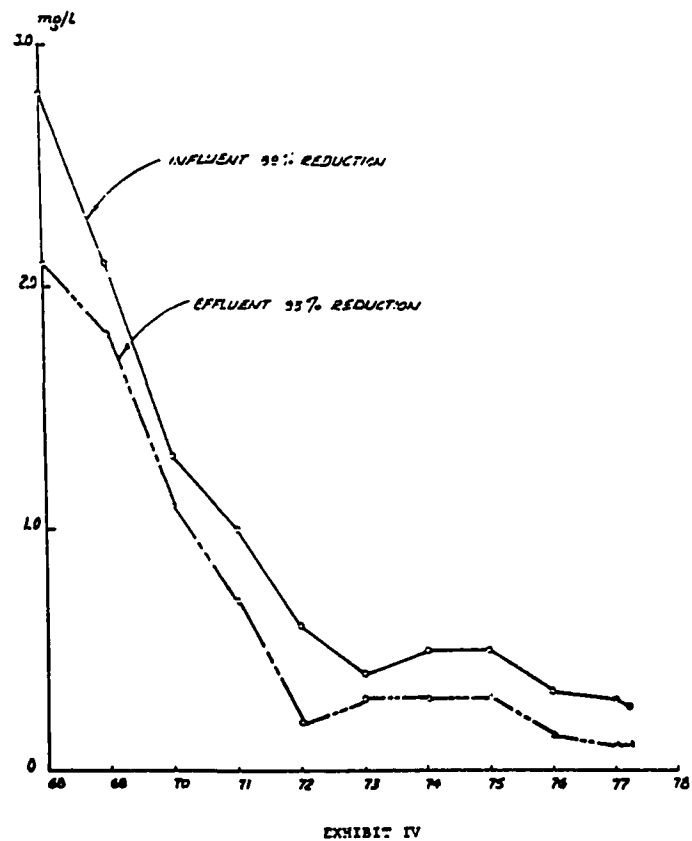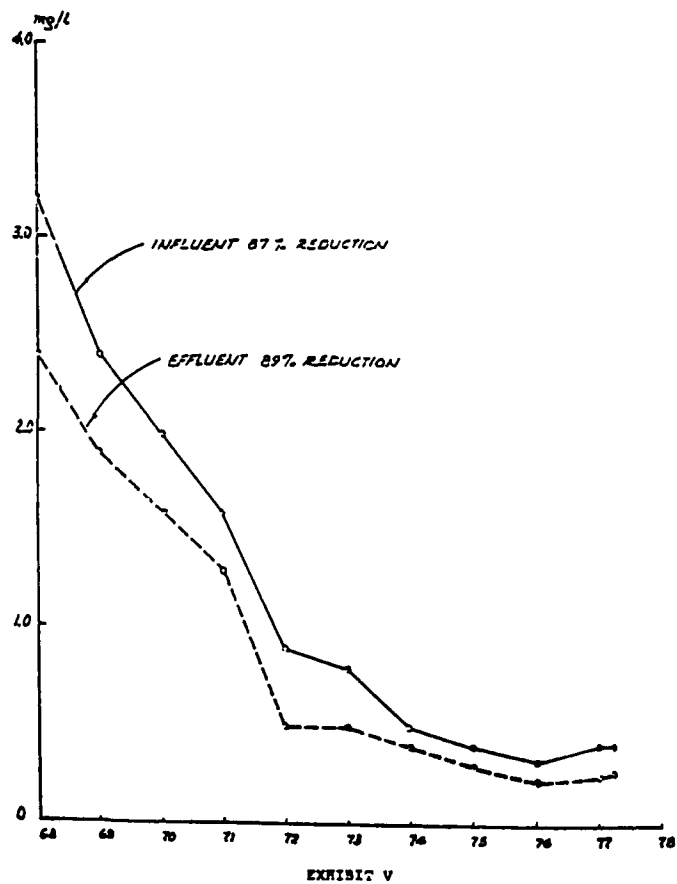

TOTAL METAL IN SEWAGE

EXHIBIT I

TOTAL CYANIDE IN SEWAGE
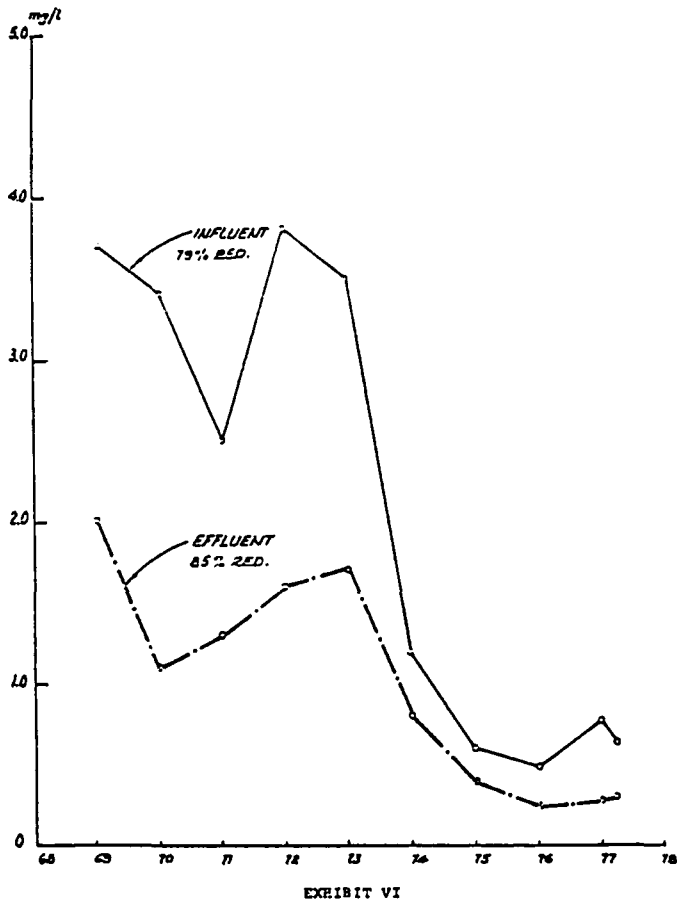

INFLUENT 92% REDUCTION

EFFLUENT 96% REDUCTION

EXHIBIT II

TOTAL CHROMIUM IN SEWAGE

INFLUENT 90% REDUCTION

EFFLUENT 96% REDUCTION

EXHIBIT III

TOTAL COPPER IN SEWAGE

INFLUENT 92% REDUCTION

EFFLUENT 93% REDUCTION

EXHIBIT IV

TOTAL NICKEL IN SEWAGE

INFLUENT 87% REDUCTION

EFFLUENT 89% REDUCTION

EXHIBIT V
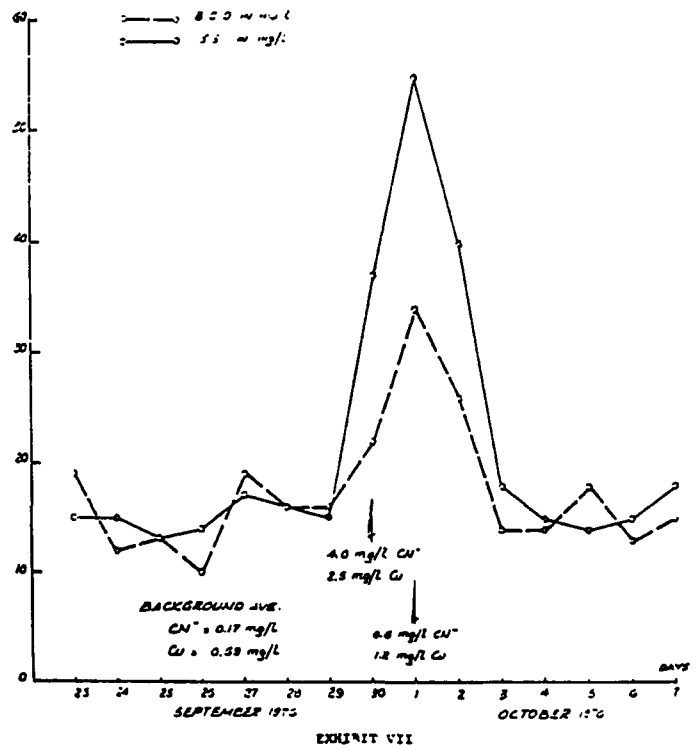
60

TOTAL ZINC IN SEWAGE

EXHIBIT VI

The idea of non-linear removal efficiency can best be shown by comparing the removal of each metal at the higher influent levels of pre-ordinance to the lower concentrations after pretreatment enactment. Percent removals were as follows:
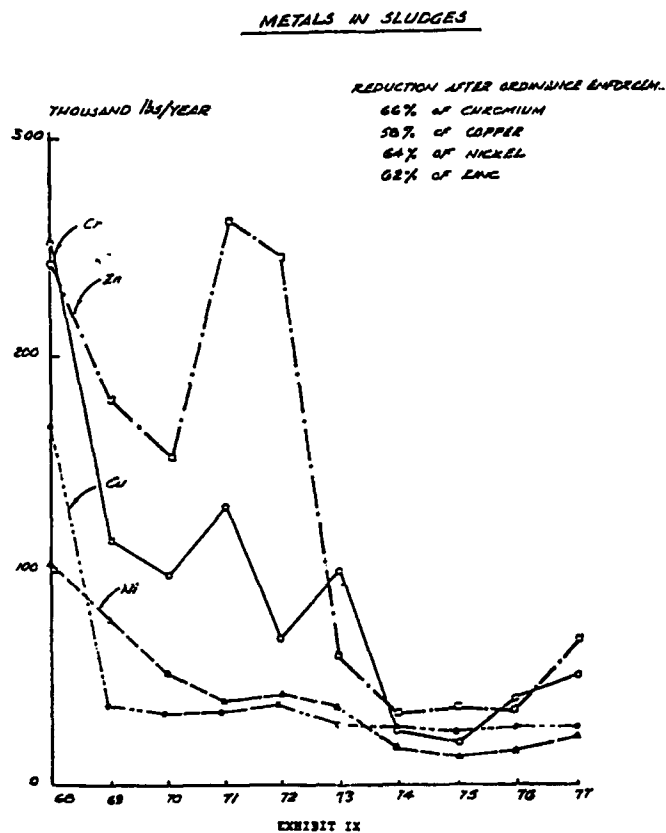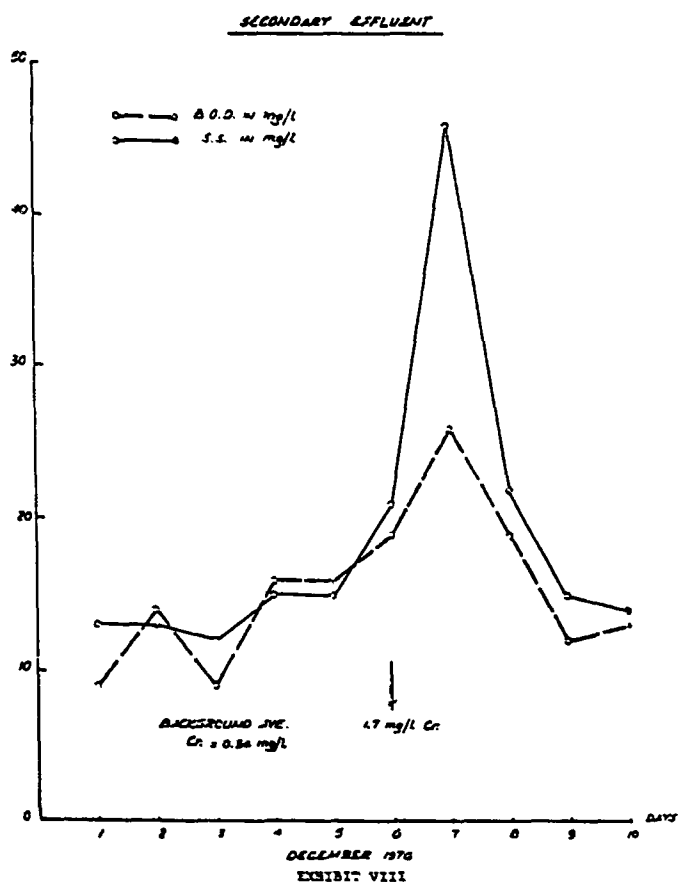
	Before	*After*
Cyanide	43% of 2.1 mg/l	71% of 0.14 mg/l
Chromium	35% of 5.1 mg/l	73% of 0.49 mg/l
Copper	25% of 2.8 mg/l	63% of 0.30 mg/l
Nickel	25% of 3.2 mg/l	38% of 0.42 mg/l
Zinc	46% of 3.7 mg/l	63% of 0.78 mg/l

These figures show conclusively that higher removal efficiencies are obtained at the lower influent concentration. Also, as expected, nickel exhibits the lowest removals of all in a wastewater treatment plant.

Slug discharges are common to any batch operation. These short but very concentrated discharges can have adverse effects on a wastewater treatment system, particularly biological systems. Typically, treatment efficiency is impaired for times ranging from minutes to days. Exhibits VII and VIII show examples of large slug discharges and the effect on treatment as measured by suspended solids and BOD in the effluent. In each case the concentration of metal is the average (composite sample) concentration for the day, not the instantaneous level which probably was an order of magnitude larger. Prior to the pretreatment ordinance, such occurrences were common and background levels were continuously

is even more dramatic, with reductions of 93% for influent and 96% for effluent.

Chromium is illustrated in Exhibit III and shows excellent reductions of 90% and 96%. Copper is shown in Exhibit IV and has reductions of 89% and 93%. Nickel appears in Exhibit V and shows reductions of 87% and 89%. Zinc displays erratic changes in Exhibit VI, but shows overall reductions of 79% and 85% for the influent and effluent respectively. Zinc is an example of interdisciplinary effects.

In 1970, air pollution control requirements forced brass foundaries to install scrubbers to remove zinc oxide from their air stacks. This waste material was then discharged into the sanitary sewer system, causing zinc concentrations to rebound to previous levels. City staff then focused energy on methods of achieving pretreatment that would reverse this trend and by 1973 levels of zinc in the sewage system plummeted.

Relative reductions between influent and effluent show that even though lower concentrations were originally present in the effluent, higher reductions were obtained. This was observed for all metals and cyanide. It appears that municipal treatment plants are capable of removing or treating low levels of metals but that efficiency decreases with increasing influent concentration. Nickel has often been described as the metal having lowest removal, a view supported by our data that show the smallest difference in improvement at two percent.

SECONDARY EFFLUENT

EXHIBIT VII

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EXHIBIT VIII

EXHIBIT IX

higher. Currently, however, cases such as Exhibits VII and VIII are rare.

Much of the influent heavy metal passes through municipal treatment, but much is also trapped in the process and removed with the sludge. Until Grand Rapids changed to a heat treatment system, this sludge was digested. The reason for changing was due to the undependability of anaerobic digestion caused by industrial chemicals.

EPA has required wastewater treatment operations to consider other than "standard treatment" of sewage and sludge, the end product. Land application of sludge has become more feasible in Grand Rapids as metal content in sludges continues to decrease, as illustrated in Exhibit IX. The reductions average 66%, resulting in sludge that contains only about one-third the amount of heavy metal compared to pre-ordinance levels. Agricultural use of sludge could prove worthwhile both in resource recovery efforts and in reducing costs of incineration.

Water Quality Improvement

The greatest direct public benefit resulting from the industrial waste control program has been the revival of the Grand River. For many years, the Grand River served as an open conduit for transporting industrial wastes from Grand Rapids to Lake Michigan. The public attitude toward the River was one of almost total disrespect. Few persons used the Grand as a recreational resource and fewer yet dared eat the fish caught from its waters.

In 1972, the flow of industrial wastes into the Grand had slowed to a mere fraction of its former volume. In the Spring of that year, the Michigan Department of Natural Resources selected the Grand as a place to stock Steelhead Trout along with Coho and Chinook Salmon. These fish would migrate to Lake Michigan to feed during the summer months when the river warmed to intolerable temperatures for these species to survive. The Steelhead Trout return to the river to spawn in the Spring while the Salmon begin their spawning in the Fall months.

By 1974, the Trout and Salmon spawning runs started to attract a lot of attention from local fishermen. Trout weighing as much as 15 pounds and Chinook Salmon up to 35 pounds were common catches below the dam in downtown Grand Rapids. First a few, then hundreds of fishermen were participating in this newly-created fishery usually limited to northern clear water rivers. The local Chapter of the Izaak Walton League of America sponsored a Trout fishing contest within the City limits of Grand Rapids to help promote our revived water resource.

Development of the fishing in the Grand River was only the beginning. Canoeing enthusiasts began promoting and mapping the river as an enjoyable canoeing adventure. Construction and improvement of boat ramps brought more and more boating enthusiasts. More park land was purchased by the City and was developed into recreational areas that added important

green belts along the banks of the river. Hundreds of persons began enjoying the parks. Environmental groups gathered together to clean the river banks of littered debris.

In 1976, a fish ladder was constructed at the dam in downtown Grand Rapids for the purpose of passing fish upstream into the Grand and its many tributaries. On top of this fish ladder a sculpture was placed that was created by a local artist and financed by some $75,000 in local donations. Alongside the fish ladder and sculpture there was created a unique little park for the benefit of those persons watching Trout and Salmon "climbing" the fish ladder. As many as two hundred noisy participants are often present to cheer the fish as they find their way up the ladder.

The future of the Grand River as a recreational resource appears to be almost unlimited. Additional parks are being planned for development and many recreational activities are often centered on or near the river. The public attitude toward the Grand River has been converted to one of appreciation and respect in just a few short years.

Selecting the Proper Unit Processes
For the Treatment of Electroplating Wastewaters

A. F. Lisanti & S. O. Megantz*

INTRODUCTION

In order to design a successful waste treatment facility for what can be relatively complex electroplating treatment problems, the Owner, Engineer and Regulating Agency cannot depend upon a simplistic, cookbook approach to the required treatment processes and equipment. The textbook processes or prepackaged simplified treatment units may be the optimum treatment for a specific electroplater's operation, but that fact should be proven before all assume it is so.

An Engineer's responsibility to the Owner and the Regulatory Agencies is not to complicate what at times can, in fact, be a straightforward physical/chemical treatment process. However, he must exercise good judgement and provide a workable system that will achieve the desired results. We believe that such sound judgement would require a demonstration that what is proposed as a solution will in fact work.

This paper presents what we believe to be a proper engineering approach to selecting unit processes for the treatment of electroplating wastewaters. The actual work required per project will, of course, vary dependent upon information obtained and problems encountered. Our experience has demonstrated that a systematic, test-the-theory approach does result in successful projects that achieve the desired results.

We do not imply that this is the only right way, for we have seen successful projects that utilize the "design it big and flexible" principle, or that hit upon constituents that react exactly as per the textbook, and the prepackaged process worked. The approach we present is admittedly conservative, but it should not fail.

The first phase is the development of a preliminary concept; this is the investigation, problem definition and presentation of solutions. Next is the testing of the possible solution by treatability studies, followed by designing a custom facility. Finally, the facility must be constructed, operators trained, and the plant performance monitored to assure that the desired results are achieved.

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Industrial Waste Division & Real Estate/Construction Operation
The Chester Engineers, Inc. & General Electric Company

PRELIMINARY CONCEPT PHASE

The Engineers are normally engaged to conduct field investigations and make recommendations relative to wastewater treatment facilities to bring the Electroplater-plant discharges into compliance with the National Pollutant Discharge Elimination System (NPDES) Permit or national/local government pretreatment requirements.

The field investigations include field locating all known discharges of wastewater. In conjunction with the "in-plant" survey, a flow monitoring and sampling program is conducted in the sewer systems located throughout the plant. This information is used in the development of a flow and pollutant mass balance for the plant. A sampling program should also be conducted during the peak period of plating operations. This information is then used to develop a flow diagram of the existing wastewaters and to establish design loadings (both relative to flow and pollutants) for the required wastewater treatment facilities.

Electroplating wastewaters contain a combination of pollutants that are not compatible for practical treatment methods. It is normal to segregate the waste stremas relative to pollutant content so that practical treatment methods can be employed. Therefore, the proposed segregated waste streams should be simulated in the laboratory for use in waste characterization and eventual treatability studies. We believe this is necessary to assure that each stream has compatible constituents and waste treatment is not an unnecessary complication, for we have all fallen victim to "end of pipe" treatment where chromium is in alkaline streams; metals and cleaners are combined; and oils plus solvents are everywhere.

A study of water conservation is also performed so that the volume of wastewater requiring treatment might also be reduced.

Concentrates are always a candidate for segregation. The segregated waste streams can normally be divided into six categories:

(1) Chemical Oxygen Demanding (COD) Waste
(2) Chrome Waste
(3) Cyanide Waste
(4) Acid-Alkali Waste
(5) Sanitary Sewage
(6) Non-Contact Process Water

However, it is often necessary to further define the acid-alkali waste to metal bearing, cleaners, oils, and inert solids to achieve present effluent requirements and/or go to wastewater recycle. If possible, the COD waste should be directed to the sanitary sewer system because its waste constituent composition can be compatible to sanitary treatment. Non-contact process waters can be recyled or discharged withoug treatment, provided the thermal load is not a problem.

The baseline for a successfully engineered project is water conservation and waste stream segregation.

Water Conservation

The amount of water presently used in plating rooms is often excessive and requires conservation. Methods of conservation should be suggested to the user and trial use of these methods initiated by plant personnel. The volume of wastewater requiring treatment can be reduced significantly by employment of water conservation procedures. This is particularly true if the existing wastewaters resulting from the plating of metal parts are divided into two streams: the acid waste line and the alkaline waste line. Analyses of these waste lines often reveal chromium and cyanide present in both lines. The dilution of the chromium and cyanide waste with other wastes which do not contain these parameters require high chemical treatment dosages to meet present and future effluent requirements.

A number of approaches can be taken to determine the amount of water that could be saved. These can include automatic plating machines, rinse flow control valves, countercurrent and still rinsing. The formulae and results of these physical changes are well documented in the literature.

One very simplified approach we use to demonstrate possible over rinsing involves comparison of the dissolved solids concentrations of the acid and alkali waste lines during different shifts. It is usually seen that the water usage rate during "slack" periods can be reduced to maintain a dissolved solids level equal to or less than the active periods. Averaging the dissolved solids concentration of each shift for each segregated line can permit calculating the percent reduction possible.

On one project the analysis of possible flow reductions was based upon the peak rinse tank concentrations and areas plated determined by field studies. We were able to demonstrate a water consumption which could be reduced to an average of approximately 7.0 gallons per square foot plated compared to the existing rate of approximately 61 gallons per square foot plated. This rate is still high when compared to EPA's guideline of 3.93 gallons per square foot. However, it was practicable to achieve the 7.0 gallons per square foot rate. Further reductions were just not possible because of the multiple and varied processes employed in this plating room.

Waste Stream Segregation

Each waste is reviewed and categorized with respect to its chemical composition. If there is a typical system, it is one where the chrome waste consists of chromium rinses and cooling tower blowdowns and the cyanide waste contains all of the rinses following cyanide baths. The acid/alkali waste generally contains all of the remaining rinses from the plating room, which include mostly acidic and alkaline solutions of metals. The deionizer backwashes and deburring equipment rinses are also included in the acid/alkali waste line. The wastes containing COD can be considered sanitary in nature rather than industrial and, therefore, discharge to the sanitary sewer system if available.

Waste Character

The range of concentrations and quantities of waste contaminants can be determined by (1) sampling and analysis of sewer streams, (2) determining "peak" concentrations found in each rinse water sample in conjunction with the projected design flow, and (3) simulating the projected wastes in the laboratory and performing an analysis of each.

The quantities determined by the first method require a proper interpretation of mass balance and projections. The second and third methods can be used to project future waste character.

The quantities found by the third method usually represent the high end of the range. Because one may propose to segregate the existing waste streams even further, the projected waste streams for the treatability studies are nomally simulated. The Engineer must rely upon plant personnel to supply sufficient information to undertake this task. The projected production figures for each individual plating room tank and the results from drag-out studies are the criteria used to establish a baseline. By using the average daily production rates for each tank in conjunction with an established drag-out coefficient in ml per square foot plated, an approximation of the average volume of concentrate "dragged out" of each production tank into the succeeding rinse tank is calculated. Using the projected flow rates for the design year, calculations are made for the volumes of concentrates required relative to the volume of rinse water. The analyses of these wastes represent the high range.

The mass balance approach to waste characterization is most typical. A mass balance of the various waste streams can be determined from data collected during a wastewater survey program. The balance compares all flow and constituent loads from individual sources with the plant outfall. This approach requires engineering judgement to assure that "bad" day and variations are properly bracketed.

TREATABILITY

Field Treatability Studies

If the wastes are properly separated, it is often advantageous to conduct treatability studies of the waste lines during the field survey:

(1) The acid and alkali requirements for pH adjustment of the alkali and acid lines can be determined first.

(2) The sodium metabisulfite required to reduce the hexavalent chrome in the acid line and waste chromium concentrates can be measured. Various dosages of sodium metabisulfite and varying retention times can be evaluated.

(3) A sample of the alkali waste line can be analyzed for amenable cyanide concentration and cyanide, if present, can then be treated with chlorine to remove the amenable cyanide. Various dosages of chlorine and varying retention times can be evaluated.

The alkali and acid requirements determined in the field or batch studies indicate several important factors such as buffered condition of each stream, unusual usage or reactions, potential problems, etc.

If both the acid and alkaline lines are neutral to basic, the treatment for chromium reduction at low pH values proves unattractive from a chemical consumption (both acid and alkali) and total dissolved solids standpoint. Field investigations into hexavalent chromium reduction using sodium metabisulfite could reveal this fact. For example, at the General Electric Waynesboro Plant, removal of hexavalent chromium to <0.05 mg/l Cr^{+6} required a sodium metabisulfite dosage of 36 pounds $Na_2S_2O_5$ per one pound Cr^{+6}. Theoretical dosage for removal is about three pounds $Na_2S_2O_5$ per one pound Cr^{+6} Because this chemical is a reducing agent, any dissolved oxygen present in the waste also presents a chemical demand where one pound dissolved oxygen requires about four pounds sodium metabisulfite. This excess use of chemical reducing agent as well as high acid/alkali requirements indicated a need to review alternative treatment schemes and/or collection facilities for chromium treatment.

At the same plant, alkaline chlorination studies for the alkaline line waste revealed that a slight improvement in effluent quality with respect to cyanide could be obtained by increasing contact or detention time from thirty to sixty minutes. Improvement of treatment efficiency was seen by increasing solution pH from 9 to 10. For complete oxidation of amenable cyanide (below 0.05 mg/l CN^-), a dosage of 112 mg/l Cl_2 or eight pounds Cl_2 per one pound CN was required. This value is significantly higher than the theoretical requirement of three pounds Cl_2 per one pound Cn. This high consumption rate is due at least in part to the fact that caustic cleaning solution rinses are mixed with cyanide waste streams. Further investigation into that occurrence was warranted.

Field treatability studies are most practical when an existing waste facility needs to be modified and upgraded. Often one finds an existing cyanide oxidation plant with chlorine residual and amenable cyanides in the effluent, symptomatic of improper treatment. Treatability studies can prescribe the solution to this common problem.

Laboratory Treatability Studies

The laboratory is usually the best place to establish design parameters and to test the treatment process flowsheet. One should always consider the so called "worst case" situation. This often removes the element of surprise when a treatment plant is placed on-line. Typical studies include:

(1) **Chromium Reduction** - Review a cross-section of alternative treatment methods including the use of waste concentrates. Recovery should be evaluated.

(2) **Cyanide Oxidation** Evaluate alkaline chlorination which is frequently used. Design requirements can be high variant. Electrolytic treatment of concentrates should be considered.

(3) **Quiescent Settling** Determine settling rates, flocculation requirements, sludge production, and requirements for settling aids.

(4) **Oil Treatment** - Investigate acid/heat, alum/acid, acid/alkali, etc. Soluble oil often requires the investigation of ultrafiltration and reverse osmosis processes.

(5) **Chemical Reactions** - Set proper reaction time, agitation, and reagent quantities.

(6) **Filtration** Determine liquid and solids loading rates as well as permeate quality and sludge dryness.

(7) **Leachate Analyses** - Measure the characteristics of the sludge generated by treatment (now a significant criterion).

(8) **Reuse and Recovery** processes.

It is not our intent to leave the impression that we are advocating a complete spectrum of testing for all electroplating wastewaters, although this may be prudent for the neophyte. We believe that the skilled Engineer and Owner will readily determine the optimum testing required for a successful project.

One purpose of treatability studies is to determine if the contaminants found in the waste flow can be reduced to satisfy the requirements of the regulatory agencies. Hopefully, the studies will be conducted prior to agreeing upon effluent quality criteria.

Design Phase

By utilizing proper scale-up factors the Engineer can proceed from study to design. It is usually advisable to view a number of alternative treatment processes.

We find it helpful to develop a preliminary performance specification for each of the major equipment items. Vendors are requested to submit pre-qualification information with preliminary pricing. That information can include performance guarantees. This is most helpful in evaluating alternative unit processes. The alternatives should be subjected to a review by the client. once the desired alternative is selected, then the Engineer can prepare process flowsheets.

Desires of the user relative to degree of automation, operating period of the plant, aesthetics, design/construction standards, etc., must be incorporated into the design.

Design must recognize and address the details of chemical and solids handling, corrosion protection, fume abatement, reliable field instrumentation, monitoring, safety, and hydraulics to have a successful project.

Construction/Start-Up

The engineering aspects of this phase require a monitoring of equipment and installation to assure that the design intent is not violated. We believe the manufacturer should be relied upon to assure his equipment is installed properly and certify that it is ready for service. His knowledge, if properly orchestrated, can be of great value in the successful project. This can be a specification item to assure there is sufficient money in the project to accomplish it.

Start-up should be performed by experienced personnel. This period can be used as an opportunity to train personnel that will eventually operate the facility.

Equipment and process should be tested once the mechanical, electrical, and instrumentation operation is satisfactory. Tests should assure that design and guarantee conditions are achieved. Test results are often a key input toward improved operation of a particular facility and improved design for the next plant.

Plant performance should be monitored, for few if any plating shops remain static with respect to wastewater discharge; thus, new plating processes can alter treatment performance. Ideally, the plater will consider the consequences to the treatment facility before adopting a new plating process.

SUCCESSFUL PROJECTS

Our engineering approach to three electroplating operations of the General Electric Company was essentially as outlined in this paper. However, our studies revealed unique problems in each plant; thus, the unit treatment processes for each plant differed. We are convinced that a simplistic approach to each treatment project would have failed to achieve the desired results.

Charlottesville, Virginia

The General Electric Charlottesville facility manufactures printed circuit boards. In so doing, wastewaters are generated from both electrolytic and non-electrolytic plating processes. A batch type of treatment system was recommended because of small flows and complex wastes. The system provides for scavenger hauling of certain bath concentrates. The remaining bath concentrates, such as the acids, would be metered into and blended with the rinse wastewaters for treatment. The treatment process consists of a lime addition to pH 11 followed by a sulfide addition and filtration through a diatomaceous earth medium. The diatomaceous earth filter would both remove the precipitate and dewater the solids. The filtrate would be neutralized with sulfuric acid to pH 8.5 before discharge.

The proposed facility meets all of the prescribed effluent requirements except for fluorides. The wastewater contains fluoborates, and no known practical treatment technology exists for the removal of fluoborates. Consequently, while the proposed system would reduce the fluoride ion concentration such that it would conform to the fluoride concentrations specified in the effluent limitations, it would not remove fluoborate ions which are analytically measured as part of the total fluoride concentration. As a result, we suggested that since fluoborates are stable compounds and cannot be removed by best practical treatment technology, the effluent limitation should differentiate between fluoride and fluoborate ions.

Another problem was the fact that lime addition alone did not sufficiently precipitate the copper content of the wastewater; lime coupled with a sulfide addition was investigated. These investigations demonstrated that by incorporating sulfide into the lime addition process, the copper concentration would be lowered sufficiently to meet the proposed effluent limitations. To determine the amount of sulfide required for this removal, various amounts of sulfide were added to the wastewater collected during selected copper operations and the residual soluble copper concentration measured. These evaluations illustrated that approximately 1.5 times the stoichiometric amount of sulfide, based on the dissolved copper concentration at pH 11, is required to lower the copper concentration to less than 0.5 mg/l. Moreover, the studies demonstrated that the sulfide addition would not only reduce the copper concentration at an elevated pH of 11, but also at a pH of 8.5. The fluoride ion concentration of the wastewater, however, affects the pH used. Although sulfide addition at pH 8.5 may be used to precipitate the metallic constituents, at this pH value the fluoride concentration may not be lowered sufficiently to meet the required fluoride ion concentration. Therefore, precipitation at pH 8.5 may not always produce an effluent quality which would conform to the effluent limitations.

Treatment Process

Essentially, the process consists of a batch treatment system. Two batch treatment tanks are provided. Each contains an agitator and each is sized to handle one day's flow. As one tank is filling, the wastewater in the other tank is treated and pumped to the other unit processes.

In the treatment process the concentrates that are presently scavenger hauled continue to be disposed of by an outside vendor. Therefore, as the baths are dumped, they flow to a 5000 gallon storage tank prior to disposal. The remaining concentrates that are presently dumped into and mixed with the rinses flow by gravity to another 5000 gallon concentrate waste holding tank. At a rate of some 200 gallons per day, these concentrates flow to one of the two batch treatment tanks. Simultaneously, the rinses which flow by gravity from the manufacturing processes at about 50 gallons per minute also enter the same batch treatment tank.

Once the wastewaters are collected in one of the batch treatment tanks, the contents are agitated and the pH raised to 11 with lime. This lime addition normally amounts to about 53 pounds $Ca(OH)_2$ per day and is controlled by a pH assembly unit. After the lime is added, some 6.3 pounds per day of sulfide (62.7 pounds per day

TABLE 1
REMOVAL OF COMPLEXED COPPER
(AND OTHER METALS)
FROM ELECTROPLATING WASTEWATERS

- Location: Charlottesville, Virginia
- Lime added to pH 11
- Sodium sulfide added to equivalent
  sulfide ion concentration of 20 mg/l

Metal	Untreated Wastewater (mg/l)	Treated Wastewater (mg/l)
Copper	17	0.4
Nickel	0.30	< 0.2
Lead	1.85	< 0.2
Zinc	0.86	0.4
Tin	4.29	< 1.0

$Na_2S \cdot 9H_2O$) are added. The tank contents are then analyzed for such constituents as soluble copper, tin, or zinc. If these analyses indicate concentrations that are acceptable for discharge, the unsettled slurry is pumped to a diatomaceous earth pressure filter.

Prior to entering the filter, a diatomaceous earth slurry (body feed) is mixed with the wastewater. This addition prevents blinding of the filter and maintains an acceptable filtration rate. Although this body feed addition could be adjusted in the field, it is estimated that about one pound diatomaceous earth per pound suspended solids is in the pH adjusted wastewater. This equates to about 29 pounds of diatomaceous earth per day. In addition, diatomaceous earth is used to precoat the filter. The filter is emptied and precoated once a week.

The effluent of the filter flows to an effluent tank where under pH control, some 27.5 pounds per day of sulfuric acid are added to adjust the pH to 8.5. The effluent of this tank is discharged to the stream.

Since the pressure filter is designed to process a one day flow of wastewater in a four hour period, it is not used the remainder of the day. To prevent the diatomaceous earth precoat from falling off during periods when the filter is not in use, and to conserve the amount of diatomaceous earth used in the process, a flow must be recirculated through the filter. This flow originates at the effluent tank and is pumped through the filter and returned to the effluent tank. This technique permits the filter to be emptied and precoated once a week. Consequently, at a solids content of fifty percent some 780 pounds or 11.2 cubic feet of cake must be disposed of per week. Based on our treatability studies, the expected effluent quality of this treatment process is listed in Table 1.

Waynesboro, Virginia
General Electric's Waynesboro, Virginia plant is engaged in the manufacture of data handling equipment. There are many small cleaning and plating operations at this plant. It afforded the best opportunity for water

conservation and waste separation. An existing treatment plant was operating and achieving reasonable results; however, the processes could not satisfy the new requirements. We judged that we could utilize the existing settling lagoons as waste equalization tanks; other tanks could be used for waste storage. All treatment processes were abandoned. Specific unit processes include the following:

Chromium Reduction System
The segregated chromium wastes have a hexavalent chromium concentration of 15 mg/l. Electrochemical treatment with raw concentrates bled into rinses offered the lowest combination of initial capital investment and operating costs of any of the treatment methods considered. Disposal of the waste chrome concentrates in a secure landfill or evaporation in a solar evaporation pond was not practical in terms of cost.

The electrochemical unit is commercially available, and utilizes sacrificial iron electrodes. It produces a lesser amount of dissolved solids than the other alternatives, which is an asset to possible future water reuse considerations. However, a small additional volume of sludge will be produced because of excess iron hydroxide formation (approximately ten pounds dry per day more solids). This volume of extra sludge is insignificant in terms of operating costs because of its relatively small volume. The unit also provides slight removal of other metals during its operation.

The unit operates most efficiently at pH values of 6 to 9. The treatability results indicated that the pH of the waste would be in this range. However, because the chrome concentrate is acidic, a caustic soda feed system would be minimal. Therefore, we concluded that the chrome concentrate could be bled into the rinse stream.

Treatment results are presented in Table 2.

TABLE 2
ELECTROLYTIC REDUCTION OF
SEGREGATED CHROMIUM (+6) WASTEWATERS

- Location: Waynesboro, Virginia
- Concentrates bled into main chromium rinse stream
- Chromium (+6) reduced electrolytically at pH 6 to 9

Parameter	Untreated Wastewater (mg/l)	Treated Wastewater (mg/l)
Chromium (+6)	13.7	< 0.05

Cyanide Oxidation System
The concentrates amounting to fifty gallons per day (gpd) and containing 36,000 mg/l CN "A" are treated in an electrolytic destruction unit and then bled into the rinse system.

In comparing all of the alternative treatment schemes,

the treatability results revealed only small differences in the amount of amenable cyanide left with that remaining in the alkaline chlorinated effluent after thirty minutes of single stage oxidation. The concentration of total cyanide was higher when the treated cyanide concentrate was bled into the rinse stream before chlorine oxidation. However, after mixing the treated total cyanide wastes with the other wastes and raising the pH, the total cyanide concentration met effluent limitations.

Treatment results are set forth in Table 3.

TABLE 3
TREATMENT OF CYANIDE WASTEWATERS

- Location: Waynesboro, Virginia
- Amenable cyanides in concentrated solutions electrolytically oxidized
- Oxidized concentrates bled into main cyanides stream for conventional oxidation by chlorination

Parameter	Untreated Concentrates (mg/l)	Treated Concentrates (mg/l)	Treated Blended Stream (mg/l)
Total Solids	284,380	200,900	
Total Cyanides	38,400	1,260	~3
Amenable Cyanides	36,000	<0.05	0.35*

*Upon precipitation and solids removal this reduces to <0.05 mg/l.

Combined Waste Treatment System

Initial treatability results showed that the pH must be raised to about 11.0 for sufficient precipitation of metal hydroxides to meet effluent limitations for metals (nickel, in particular). Also, phosphorus (that is, ortho-phosphate) removal was enhanced at this high pH value.

The data in Table 4 shows the beneficial effects of polishing filtration at a pH of 11 on metals removal and, in particular, the enhancement of nickel removal. This led to the inclusion of polishing filtration in the treatment process.

The data in Table 5 shows the quality of wastewater containing treated chromium and cyanide wastes when filtered at a pH of 9.5. Orthophosphate removal was satisfactory but zinc and nickel concentrations were at borderline values. It was concluded that good pH control in the 9.5 to 11 range would be required to minimize lime consumption and to achieve the necessary heavy metals removal.

Our studies indicated that lime requirements and sludge production would be significant. These problems prompted additional study.

To improve upon the initial recommended treatment system and to decrease the volume of sludge to be disposed of, a sludge dewatering study was performed. This consisted of clarifying the combined wastewater and gravity thickening the sludge with 2 mg/l of coagulant aid

TABLE 4
REMOVAL OF COMPLEXED NICKEL
(AND OTHER METALS)
FROM COMBINED
ELECTROPLATING WASTEWATERS
EFFECT OF POLISHING FILTRATION

- Location: Waynesboro, Virginia
- Lime added to pH 11
- Solids removed by settling, then filtration through diatomaceous earth

Parameter	Settled Waste (mg/l)	Filtered Waste (mg/l)
Copper	0.41	0.29
Nickel	1.3	0.10
Total Chromium	0.14	N.D.*
Zinc	0.14	0.04
Tin	1.0	N.D.*

*N.D. = not detected.

TABLE 5
REMOVAL OF COMPLEXED NICKEL
(AND OTHER METALS)
FROM COMBINED
ELECTROPLATING WASTEWATERS
EFFECT OF TOTAL TREATMENT

- Location: Waynesboro, Virginia
- Lime added to achieve pH 9.5
- Solids removed by settling, then filtration through diatomaceous earth

Parameter	Untreated Waste (mg/l)*	Treated Waste (mg/l)
Nickel	7.2	0.5**
Iron	7.6	0.32
Copper	1.12	0.13
Zinc	2.9	0.04
Ortho-Phosphate	12	0.01

* This waste contains previously reduced chromium (+6). Amenable cyanides were previously oxidized.
**Other studies showed concentration reductions to 0.1 mg/l by increasing pH to 11. See Table 4.

added prior to mechanical dewatering by use of a filter press.

It should be noted that this sludge comprised the total solids to be disposed of because the solids (and diatomaceous earth) from the pressure filters used to polish the clarifier overflow were also fed to the gravity thickener.

Gravity thickening increased the solids concentration of the clarifier sludge from one to two percent by weight. The filter press dewatered the thickened sludge at a rate of 3.7 gallons per hour per square foot with a cycle time of one hour and produced a sludge cake containing thirty percent solids.

Filtration rates in pressure filters used to polish clarifier overflows are high when compared with presses in sludge filtration service. The rates decrease markedly as a significant cake thickness (1/16 inch) builds up in the filter. The final design filtration rate for pressure filters in this type application has been found to be about 0.5 gallons per minute per square foot of filter area. When the filter reaches this rate, the cycle is terminated and the cake is discharged. This study indicated that a cycle period of eight hours is reasonable. The resulting cake thickness would be about one-fourth inch, including one-eighth inch precoat.

TABLE 6
ANALYSIS OF EFFLUENT

	Untreated Combined Wastewater Mixture*	pH Adjusted Effluent
pH	5.9	9.0
Alkalinity to PHT, mg/l CaCO₃		12
Alkalinity to M. O., mg/l CaCO₃		70
Acidity to PHT, mg/l CaCO₃	94	
Acidity to M. O., mg/l CaCO₃	340	
Total Solids	1220	1350
Suspended Solids, mg/l	24	1
Dissolved Solids, mg/l	1196	1349
Iron, mg/l Fe	7.4	0.33
Manganese, mg/l Mn	1.4	0.02
Nickel, mg/l Ni	8.0	0.10
Copper, mg/l Cu	3.2	0.38
Hexavalent Chromium, mg/l Cr	0.00	0.00
Total Chromium, mg/l Cr	1.46	0.04
Zinc, mg/l Zn	3.05	0.06
Lead, mg/l Pb	0.1	<0.01
Tin, mg/l Sn	0.9	0.1
Cadmium, mg/l Cd	0.01	<0.01
Fluoride, mg/l F	10.0	5.0
Total Phosphorus, mg/l P	16.4	2.8
Ortho Phosphorus, mg/l mg/l P	11.5	0.04
Hydrolyzable Phosphorus, mg/l P	13	0.07
Total Cyanide, mg/l CN	1.3	0.50
Amenable Cyanide, mg/l CN	0.00	0.00
COD, mg/l	58	41
Total Organic Carbon, mg/l C	29	27

*After chromate reduction and cyanide oxidation.

TABLE 7
ANALYSIS OF EFFLUENT

	Combined Waste*	Pressure Filter Effluent
Total Solids, mg/l	1317	1617
Suspended Solids, mg/l	24	0.50
Dissolved Solids, mg/l		-
Nickel, mg/l Ni	7.2	0.50
Iron, mg/l Fe	7.6	0.32
Manganese, mg/l Mn	0.8	0.0
Copper, mg/l Cu	1.12	0.13
Total Chromium, mg/l Cr		0.50
Zinc, mg/l Zn	2.9	0.40
Lead, mg/l Pb	0.06	0.05
Total Cyanide, mg/l CN	1.0	0.50
Amenable Cyanide, mg/l CN	0.0	0.00
Ortho-Phosphorus, mg/l P	12	0.01
Fluoride, mg/l F	4.9	4.0

*After chromate reduction and cyanide oxidation.

Effluent Quality

The recommended wastewater treatment facility meets all of the allowable discharge limits set forth by the State of Virginia. The final effluent quality is as set forth in Table 6 and Table 7.

Discharges Not Included
In Wastewater Treatment Scheme

The proposed wastewater treatment system does not include treatment of COD wastes or the non-contact cooling waters. The proposed system assumes the COD wastes will be discharged to the sanitary sewer system because of their waste constituent composition, none of which would have any adverse effects on a biological treatment system. The projected waste concentrations of the COD waste are presented in Table 8.

The non-contact cooling water is presently discharged directly to a nearby storm ditch which then discharges to the South River. There are no contaminants present in the waste that warrant any treatment. Therefore, there should be not objection to direct discharge in the future.

TABLE 8
PROJECTED CONCENTRATIONS
IN COD WASTE

Total Solids, mg/l	560
Suspended Solids, mg/l	100
Dissolved Solids, mg/l	460
Calcium, mg/l Ca	25
Iron, mg/l Fe	1
Total Chromium, mg/l Cr	0.1
COD, mg/l	70
Magnesium, mg/l Mg	10
Projected Total Flow For 1982	17,200 gpd

Erie, Pennsylvania

General Electric's Erie plant is engaged in the manufacture of locomotives, electric motors, and aerospace components. Supporting these operations are various plating operations; various metal parts cleaning and processing facilities; foundry operations; and an electric power station. This paper addresses the plating and cleaning operation.

This plant contains many individual manufacturing operations and waste sources spread throughout the site in individual buildings. The building survey located all discharge point sources within the manufacturing facilities. In general, most point sources in the plant have small flow rates, but their contaminants may vary from mild cleaning solutions to concentrated pickling and plating wastes. Because most of the flows are small, it may appear feasible to treat the wastes at their sources before they are discharged. Closer examination showed this is not economical. To treat each point source would in effect require a "mini" treatment plant at each source, or at the very least some type of batch treatment in the processing tank. It proved more economical to discharge to the proposed treatment system and treat compatible wastes in one single operation. There was some savings that was realized by reducing the waste volume to the treatment plant. By the use of countercurrent rinses and flow control valves, flows were reduced by 30,000 gallons per day.

After considering a number of alternatives, we decided to collect the concentrated and dilute oil-alkali wastewater in the existing concentrated oil-alkali collection system. The plating waste along with the other general plant wastes would be collected in the existing acid bearing wastewater collection system. This approach significantly reduced collection costs as compared with the separate collection of each waste. Separate collection would have allowed more efficient treatment of each category of waste collected but, in this case, this did not offset the high capital cost of achieving the separation.

The user requested that the treatment processes be designed for a fourteen hour per day operation. Design flow rates for the various wastewaters are set forth in Table 9.

TABLE 9
DESIGN WASTEWATER FLOW RATES

Description	Gallons per day (gpd)
A. Cyanide Bearing	140,000
B. Concentrated and Dilute Oil-Alkali	156,000
C. Metal Bearing (Plating)	457,000
	753,000
D. Contaminated Storm Flow (90,000 gallons treated over two days)	45,000
Total	798,000

TABLE 10
REMOVAL OF INSOLUBLE OILS
FROM SEGREGATED WASTEWATERS

- Location: Erie, Pennsylvania
- Lime added (500 mg/l) in two stages with settling after each stage

Parameter	Untreated waste (mg/l)	Treated waste* (mg/l)
Oil and Grease	392	16
Cadmium	0.55	<0.05
Chromium	0.87	0.12
Copper	0.93	<0.05
Zinc	0.68	<0.05

*After second stage.

Oil-Alkali Waste Treatment

Both the concentrated oil-alkali waste and the more dilute oil-alkali rinse waters are discharged to one of the existing 75,000 gallon waste treatment holding tanks. Pumps transfer the oil-alkali waste from the holding tank to a flash mix tank. The first step in the oil-alkali treatment sequence is that of flash mixing the waste with lime.

Lime is added in the first flash mix tank at a rate controlled by pH. With the pH adjusted to about 10 and with the proper amount of lime added, the waste flows by gravity to an oil-solids separator. The separator is sized to allow for the oil laden solids to settle to the bottom of the unit by gravity. Any free oil which floats to the top of the unit will be skimmed and transferred to an oil holding tank. The treated liquid enters a second flash mix tank where lime is again added at a dosage proportional to the first flash mix tank addition. The effluent from the second flash mix tank overflows to a second oil-solids separator, similar to the first unit for final separation of the oily solids from the liquid.

The effluent from the final separator discharges to a wastewater blending tank. In the blending tank it is combined with other waste streams and the combined streams are treated with lime for pH adjustment. The plant is designed to keep an even flow of this high pH treated oil-alkali waste to the waste blending tank. The mixing of this high pH waste with the other acidic wastes causes the resultant mixture to have an overall alkaline condition. Fresh lime then needs to be added only to trim the pH within a range of 8 to 9. Typical treatment results for the oil removal process are presented in Table 10.

The oil laden solids thicken to a sludge in the bottom of each separator. These sludges can be recycled back to the flash mix tanks to promote flocculation or can be directed to a sludge thickener for additional thickening.

Plating and General Plant Waste Treatment

Wastewater generated in the various plating operations and general plant wastewater are pumped to an existing acid brick lined holding tank agitated by an

TABLE 11
QUALITY OF COMBINED
TREATED WASTEWATERS

- Location: Erie, Pennsylvania
- Wastewaters combined after treatment: cyanide bearing, electroplating, insoluble oil bearing, contaminated storm water

Parameter	Concentration (mg/l) In Combined Treated Effluent Daily Average Values
TSS	<20
Oil and Grease	<10
Iron	1.0
Copper	0.5
Chromium	0.5
Chromium⁺⁶	0.05
Zinc	0.5
Cadmium	0.3
Amenable Cyanide	<0.05
Nickel	0.5

air mixing system. From the holding tank, the waste is fed to a chromium reduction tank where sulfuric acid is added by automatic pH adjustment. The waste in this tank is monitored for pH and ORP (Oxygen Reduction Potential). As the ORP increases, indicating the presence of hexavalent chromium, sodium bisulfite is proportionally metered to the waste. Following the reduction of chromium in the tank, the waste flows to the wastewater blending tank (the same one to which the treated oil-alkali waste flows). Lime is added to this blending tank and to a following neutralization tank to trim the pH to achieve maximum precipitation of metal hydroxides. Sodium sulfide is also added to the neutralization tank at a constant rate (0-10 ppm $S^=$). The addition of the sodium sulfide is designed to provide for additional metals removal. The majority of the metals will be removed as a result of precipitation of metal hydroxides. This formation results from the adjustment of the waste's pH. At this alkaline pH the presence of sulfide will further lower the solubility of metals through the formation of metal sulfide precipitants. Sulfide treatment has been found helpful for metals removal to achieve required effluent quality limits. From the neutralization tank the waste flows by gravity to each of two liquid-solids separators.

Prior to entry to the separators, the neutralized waste is dosed with coagulant aid in flash mix/flocculation equipment. Coagulant aid concentration is in the range of 0.5 to 2.0 mg/l. The flash mix and flocculation system is provided to properly dispense and aid and enhance formation of settleable flocculated particles. The separator units are designed to allow gravity settling of the metal precipitates which are suspended. A liquid-solids mixture first enters the separator. The suspended solids in the mixture will settle to the bottom of the unit allowing for a constant decanting of the mother liquid at

the top of the unit. The settled solids (sludge) are pumped to a sludge thickener (the same thickener in which the oil-laden solids are thickened). A second sludge pump will return, or recycle, sludge to the blending tank to improve the sludge characteristics and lower the demand for lime. The difference between a conventional clarifier and the liquid-solids separator is basically in the reduced land space requirement of the proposed unit. Both units perform the same unit process treatment of liquid-solids separation.

The clarified effluent (overflow from the separators) then flows from each separator to a water reuse basin. From there it is mixed with the treated cyanide bearing wastewater.

The final plant effluent is monitored to determine both the quality and quantity of the effluent flow. Some of this water is recycled for operations such as making lime slurry. A secondary function of the final basin is to ensure, through the use of an oil baffle, that free oil is not discharged from the system. (Table 11.)

Cyanide Bearing Waste Treatment

The existing cyanide treatment facilities provided three tanks used for holding or treating incoming wastes. Cyanides were treated in batch fashion, and discharged after settling to reduce suspended solids. The modifications included the use of sodium hydroxide in lieu of lime, the addition of automatic pH and chlorine feed instrumentation, and clarification by means of a tubular cloth media filter prior to discharge, rather than settling.

The treatment of cyanide waste is a batch process. Each batch is analyzed for cyanide prior to discharge. After the laboratory check, the tank of treated waste is pumped under flow control provided by a flow control valve to the filter. The filter removes practically all suspended solids in the waste thereby rendering it acceptable for final pH adjustment and discharge. The solid waste removed by the filter is discharged to the sludge thickener. (Table 12.)

TABLE 12
DESTRUCTION OF AMENABLE CYANIDE
IN CYANIDE WASTEWATERS

- Location: Erie, Pennsylvania
- Sodium hydroxide added to pH 9.5
- Chlorine added to oxidize cyanides
- Solids removed by small tubular filter

Parameter	Untreated Wastewater (mg/l)	Treated Wastewater (mg/l)
TSS	~10	~5
Amenable Cyanides	7.3	<0.05
Total Cyanides	7.9	0.6

TABLE 13
PLANT FILTER PRESS PERFORMANCE DATA

Location:	Erie, Pennsylvania
Percent Solids in Sludge to Filter:	2 to 4 percent
Cake Thickness (inches):	3/16 to 3/4
Percent Solids in Cake:	22% to 30%
Filtration Rate:	3 to 5 gph/sq ft to 2 lb/hr/sq ft

Sludge Dewatering Facilities

Sludge generated in the treatment of the various wastewaters is directed to a gravity sludge thickener. Because of the low solids loading rate, the sludge is well concentrated in the thickener. The concentrated sludge is removed from the thickener and pumped to a filter press. The filter press can also receive feed from pumps installed on the oily sludge tank. Sludge pumps controlled by the filter process transfer thickened sludge to the press until the head loss across the filter reaches a preset level. At that time the pump stops. The operator can then start the filter in its solids cake discharge cycle. After the solids have been removed from the press, the operator starts the press in a new filtration cycle. The filter has been sized to operate for one shift per day. To ensure proper filtering characteristics, a diatomaceous earth precoat system is included. We anticipated that when very oily sludge is being processed, the filter would first be precoated; to date, this procedure has not been necessary. Tests have shown that other filtration aids such as polyelectrolytes are not needed for this waste.

The solids cake discharged by the filter presses is put in steel bins. When full, the bins are individually trucked to a landfill. (Table 13.)

Soluble Oil Treatment and Reclamation

Waste soluble oil is collected at various locations throughout the plant site. The majority of the oil is pumped to a central storage tank. Several distant points are trucked to storage. The soluble oil waste is then pumped to the treatment plant site.

Three soluble oil treatment tanks are used to collect and treat this waste. One tank is normally available to accept untreated waste oil. When it is filled, the tank is then allowed to stand idle to allow the waste to undergo quiescent settling of suspended solids and allow free oil to float to the surface. During this settling time, the free oil is continuously removed from the surface by a rope type oil skimmer. After settling, any sludge which is deposited in the tank's bottom cone is pumped to the oily sludge holding tank. Following this preliminary treatment, prior to ultrafiltration, the tank contents are heated using steam to about 100 degrees F.

The heated waste is then recirculated through an ultrafiltration (UF) unit by a high pressure pump (one running/one standby spare) for treatment. As the soluble oil passes through the UF unit, water passes through the filtration membrane and the remaining fluid, now of a higher oil concentration, is returned to the treatment tank. This process continues until the original batch of waste oil is concentrated to about 40 percent oil. The UF unit has a nominal design of 4000 gallons per 24 hour day. The filtration process is automatic. The unit operates until a preset headloss across the UF unit is obtained. Oversized storage tanks are designed to ensure a maximum filter run. If the UF unit reaches its preset headloss before the majority of stored waste oil is properly concentrated, the partially concentrated oil would be diluted with virgin waste oil and again filtered. In this manner maximum usage of the UF unit is assured.

When properly treated, the concentrated oil is transferred to oil storage tanks. The UF unit is then cleaned using a system which employs a detergent cleaning solution circulated through the unit. Following cleaning, the unit is available for another batch of waste oil. Sizing of the UF unit is for three days per week operation. Liquid filtered from the waste soluble oil can be discharged from the unit through an effluent monitoring pit or direct to the sanitary sewer.

Based on the design figure of 12,000 gallons per week, the concentrated oil is reduced to about a volume of 600 gallons per week. In addition to de-emulsifying the

TABLE 14
REMOVAL OF "SOLUBLE" OILS
FROM SEGREGATED WASTEWATERS

- Location: Erie, Pennsylvania
- Soluble oils removed by ultrafiltration
- Permeate to sanitary sewer
- Concentrate to boiler fuel

Parameter	Untreated Waste (mg/l)	Permeate (mg/l)	Concentrate (mg/l)
TSS	400 to 2200	1 to 355	10,000 to 40,000
Phenols* (avg)	21.4	7.5	106
Oil and Grease	2000 to 17,000	300 to 700	250,000 (avg)

*As mg/l of phenol.

TABLE 15
EFFLUENT QUALITY ULTRAFILTRATION
PERMEATE SOLUBLE OIL TREATMENT PLANT

Parameter	Daily Average (3 days/week)	
	mg/l	lb/day
Flow, ~12,000 gal/wk		
Flow, ~4,000 gal/day gpd		
pH	6 - 9	-
Phenols	15	0.5
Suspended Solids	300	10
Petroleum Based Oils	5	0.17
Animal & Vegetable Based Oils	600	20

soluble oil to a concentrated oil form, the UF unit also causes the concentrated oil to become amenable to further concentration through acidification.

Reclamation of the oil concentrated by the UF unit process is proposed. The concentrated oil which is stored at another location would be periodically transferred by truck to the soluble oil treatment facilities. The oil would be placed directly into an existing concrete treatment tank now used for soluble oil acidulation. Using the existing mixer, the tank content pH would be adjusted to about 2 with sulfuric acid. Sulfuric acid could be added manually from acid carboys. After proper mixing, the oil would be allowed to stand, at which time an oil/water phase separation would take place. At this point an oil

TABLE 16
PROCESS WASTEWATER TREATMENT FACILITIES
AVERAGE EFFLUENT ANALYSES

Daily Average per Month (77/78)

Constituents	Permit Limits	November	December	January	February
Suspended Solids, mg/l	20	33.1	19.9	17.9	26.9
Oil and Grease, mg/l	10	9.5	5.4	7.0	9.5
Total Copper, mg/l	0.5	0.52	0.41	0.48	0.37
Cadmium, mg/l	0.3	0.12	0.13	0.13	0.14
Total Chromium, mg/l	0.5	0.08	0.08	0.13	0.16
Chromium, mg/l Cr^6	0.05	0.01	0.02	0.01	0.02
Total Iron, mg/l	1.0	0.61	0.55	0.67	0.68
Zinc, mg/l	0.5	0.22	0.22	0.29	0.35
Total Aluminum, mg/l	0.5	0.16	0.10	<0.1	0.10
Nickel, mg/l	0.5	0.07	0.10	0.07	0.16
pH	6 - 10	9.2	9.0	8.9	9.0
Number of Samples		24	25 - 27	30	20

TABLE 17
PROCESS WASTEWATER TREATMENT FACILITIES
EFFLUENT COMPOSITE ANALYSES

Daily Average (1/1/79 thru 1/6/79)

Constituents	Permit Limits	1/1	1/2	1/3	1/4	1/5	1/6
Suspended Solids, mg/l	20	1.0	17.5	7.5	8.0	4.0	5.5
Oil & Grease, mg/l	10	1.8	1.6	4.0	3.0	1.6	3.6
Tot Copper, mg/l	0.5	0.00	0.15	0.13	0.29	0.22	0.14
Cadmium, mg/l Cd	0.3	0.04	0.01	0.11	0.03	0.04	0.03
Tot Chromium, mg/l	0.5	0.07	0.03	0.04	0.03	0.08	0.05
Chromium, mg/l Cr^6	0.05	0.01	0.00	0.00	0.00	0.00	0.00
Total Iron, mg/l Fe	1.0	0.40	0.27	0.31	0.43	0.77	0.63
Zinc, mg/l Zn	0.5	0.04	0.04	0.04	0.04	0.07	0.07
Tot Aluminum, mg/l Al	0.5	0.45	0.31	0.23	0.23	0.21	0.39
Nickel, mg/l Ni	0.5	0.04	0.05	0.06	0.02	0.12	0.07
pH	6 - 10	9.3	7.3	8.9	8.9	9.3	8.7
Flow		188,400	502,200	492,300	369,200	662,800	192,500

decant pump would transfer the floating layer of oil to the existing elevated storage tanks. The oil would now be concentrated to about 80 percent oil, 20 percent water. The lower layer of water remaining in the treatment tank would be pumped to one of the soluble oil treatment tanks for reprocessing.

The oil-free wastewater from the UF unit is discharged to the City of Erie's sanitary sewer system. (Tables 14 & 15.)

The start-up of the treatment facility demonstrated that our engineering approach was justified. Table 16 presents the operating results during the four initial months of operation. This demonstrates some less than desirable results which could be attributed to treatment techniques. However, we were well pleased that the plant achieved a high level of compliance with effluent criteria during the start-up period.

The treatment plant has been on-line for more than one year and performance is in compliance with permit requirements. Table 17 presents the latest treatment results.

Federal Financial Assistance For Pollution Abatement

Sheldon Sacks*

I want to discuss the various important financial assistance programs that you should keep in mind when determining which route to pursue in financing your industrial pollution control equipment needs or advising clients on financing alternatives.

I would like to mention to you the tax considerations in regard to pollution control devices from certain sales, use and property taxes that allow the companies to use tax-exempt financing for their pretreatment expenditures. Such programs permit a company to pay lower taxes.

Income Tax Provisions—
(Two Alternative Tax Treatments)

Rapid Tax Amortization & Investment Tax Credit

Businesses installing pollution control equipment currently may choose between two methods of income tax treatment. Under the first alternative, the corporation chooses to depreciate the pollution control equipment over its taxable income each year for the useful life of the equipment, using any IRS-approved depreciation method, such as straight-line, sum-of-the-years-digits, or declining balance. In addition, the company is allowed to take an investment tax credit of 10%, but the credit may not exceed total tax liability, or $25,000 plus 50% of the tax liability in excess of $25,000, whichever is less. Should the allowable amount result in unused credit, this excess may be carried back to the 3 preceding tax years, and the balance still unused in those years may be carried over to the 7 succeeding tax years. The unused credit must be used in the earliest of these years and absorbed to the extent allowed. To qualify for the full investment credit, the property or equipment acquired must be depreciable, have a minimum three-year useful life, be a tangible, integral part of the enterprise's operations, and be placed in operation during the year for which the credit is sought. Structures built to house a necessary component or which are part of a component qualify for credit, although a structure built to provide shelter alone ordinary does not qualify for credit. Related mechanical equipment also is eligible even if located physically apart from the business seeking the tax credit.

Under the second alternative tax treatment, the firm may elect to take advantage of the special rapid Amortization of Pollution Control Facilities through Section 169 of the Internal Revenue code. The provision was introduced in 1969 to encourage private enterprise to cooperate in efforts to cope with the problems of industrial pollution.

Section 169 applies to a "certified pollution control facility." This is defined to be a facility completed or acquired after 1968 as a "new identifiable treatment facility which is used in connection with a plant or other property in operation before January 1, 1969, to abate or control water or atmospheric pollution or contamination by removing, altering, disposing, or storing of pollutants, contaminants, wastes, or heat, and which has been certified by the state and Federal pollution control authorities as being in conformity with applicable state and Federal regulations. In the case of a treatment facility used in connection with a plant not in operation before 1969, but in operation before 1976, only a portion of the investment may be rapidly amortized. Thus the rapid amortization provision is clearly intended to aid relatively older manufacturing operations.

In addition, eligible equipment must not significantly increase the output or capacity, extend the useful life or reduce the total operating costs of the plant or other property, nor must it alter the nature of the manufacturing or production process.

If the facilities qualify as outlined above, the taxpayer is allowed to recover the costs over a 60-month period, instead of over the longer period provided in Section 167. This 60-month amortization deduction is limited to facilities with a useful life of no more than 15 years, or that fraction of the basis of a facility with other accelerated depreciation provisions found in the code.

However, in addition to taking advantage of the rapid amortization provision, the taxpayer may also take advantage of half of the investment tax credit, or 5%, in the year in which the eligible equipment is purchased. As with the 10% credit, the same limitations to the credit allowable in any one year applies. In addition, the credit applies only to equipment with a useful life of at least five years.

Thus, if $100,000 of new facilities were acquired, the taxpayer could claim an investment credit of $5000. This amount would be a direct credit against current income taxes.

Rapid amortization is attractive only at very high discount rates or in cases where the equipment would otherwise have a useful life greater than twelve years.

*Sheldon Sacks, Financial Assistance Coordinator
EPA Office of Analysis & Evaluation
Washington, DC

Useful Life	percent of Cost of Property Qualifying for Credit
Under 3 years	0
3 yrs. or more but less than 7 yrs.	33 1/3
5 yrs. or more but less than 7 yrs.	66 2/3
7 yrs. or more	100

Aside from the tax angles for pollution control there are various Federal Financial assistance programs to help ease the cost of pollution control. The Pollution Control Loan Program was provided for in Section 8 of the FWPCA Amendments of 1972 (92-500) titled "Loans to Small Business Concerns for Water Pollution Control Facilities" and authorizes loans to assist small businesses in adding to or altering their equipment, facilities or methods of operation in order to meet the Water Pollution Control requirements established under the FWPCA. EPA must certify to SBA that the equipment is necessary and adequate to meet their pollution control requirements.

The loan program comes under the SBA Economic Injury Loan Program and during the past fiscal year 180 million dollars was appropriated for the direct loans.

An "economic injury loan" is a loan based on a hardship caused the business as a result of government regulation, namely pollution control requirements, etc. The economic injury loan program is made up of water and air pollution control requirements, coal mine, health and safety, occupational safety and health, emergency energy shortage loans, consumer protection loans, etc.

To date we have loaned out roughly fifty million dollars with the average loan being 125,000. Roughly one quarter of the loans thus far have been to electroplaters, the direct interest rate is 7⅜% and may extend for up to thirty years. Loans are made to concerns who are likely to suffer an economic injury without them: a turn down from a bank, however, is necessary in order to get the loan. (In cities with over 200,000 people, two turndowns from a bank are required.)

The loan turndown, however, may take any of a number of forms. The interest rate may be too high, the bank may require a very short payback period or the bank may require more collateral than can be met by the applicant. The bank may not want to loan that much money for a non-productive venture.

There are participation loans and guaranteed loans with SBA and commercial lending institutions, but these rates are considerably higher (participation 10¼, guaranteed loans 11¼%), than the direct loans.

Eligibility and Purpose of Loan

1. The business has an effluent discharge requiring an NPDES permit. The permit is in essence a contract between a discharger and the government. It regulates what may be discharged and how much. It sets specific limits on the effluent from each source.

2. The business emits discharges through a sewer line into a publicly owned treatment works, and the city or town requires pretreatment of the waste discharge, (The applicant must submit the municipal permit number and receive from the municipal POTW a statement detailing the specific pretreatment requirements.)

3. The business plans to discharge into a municipal sewer (307) system through the construction of a lateral or interceptor sewer.

4. The business is subject to the requirements of a State or regional authority for controlling the disposal of pollutants that might affect groundwater.

5. The business is subject to a Corps of engineers permit for disposal of dredged or fill material into navigable waters of U. S.

6. The business is subject to Coast Guard or State requirements (312) regarding the standard of performance of marine sanitation devices controlling sewage from vessels. All regulated vessels will be required to install a certified device or otherwise meet EPA standards by January 30, 1980.

7. The business is implementing a plan to control or prevent the discharge or spill of oil or other hazardous substances. (Stores oil greater than 1320 gallons above ground and 42,000 below.) (Section 311J of P. L. 92-500)

SBA DEFINITIONS OF A SMALL BUSINESS IN THE METAL PRODUCTS MANUFACTURING INDUSTRY

The Small Business Administration (SBA) has developed definitions of a small business which can be used by the SBA when granting loans. Other definitions have also been developed by SBA to be used throughout the federal government for such programs as small business set-aside contracts. Both definitions are expressed in terms of either number of employees or dollar sales volume, depending on the industry; the maximum size allowed for inclusion in the small business category also depends on the industry and varies considerably. For metal products manufacturers (all of which are a part of the 34 thru 39 series of the government Standard Industrial Classification system, of SIC code), the definitions are in terms of number of employees.

SBA defines "number of employees" as:
> the average employment of any concern including the employees of its domestic and foreign affiliates, based on the number of persons employed on a full-time, part-time, temporary, or other basis during the pay period ending nearest the last day of the third month in each calendar quarter for the preceding four quarters.

In other words, the number of employees for companies with seasonal employment is not based on the peak number. The number is an average based on the actual number at four quarterly intervals during the preceding year.

In addition, a company that conducts its business in more than one SIC must determine an employee size limit based on weighted averages. The percentage of business

performed in each SIC is multiplied by the number associated with the SIC and the results totaled for each SIC.

The accompanying Table for the metal products manufacturing SICs lists the specific company size standards used by SBA when granting loans.

TABLE I
METAL PRODUCTS MANUFACTURING SICs

Census Classification Code	Industry or Class of Products	Employment Size Standard (number of employees)
Major Group 34: Fabricated Metal Products, Except Machinery and Transportation Equipment:		
3483	Ammunition, except for small arms, n.e.c.	1,000
3446	Architectural and ornamental metalwork	250
3465	Automotive stampings	250
3452	Bolts, nuts, screws, rivets, and washers	500
3479	Coating, engraving and allied services, n.e.c.	250
3466	Crowns and closures	250
3421	Cutlery	500
3471	Electroplating, plating, polishing, anodizing and coloring	250
3431	Enameled iron and metal sanitary ware	750
3499	Fabricated metal products, n.e.c.	500
3498	Fabricated pipe and fabricated pipe fittings	250
3443	Fabricated plate work (boiler shops)	250
3441	Fabricated structural metal	250
3423	Hand and edge tools, except machine tools and handsaws	250
3425	Handsaws and saw blades	250
3429	Hardware, n.e.c.	250
3433	Heating equipment, except electric and warm air furnaces	500
3462	Metal forgings and stampings	500
3411	Metal cans	1,000
3442	Metal doors, sash, frames, molding and trim	250
3497	Metal foil and leaf	500
3412	Metal shipping barrels, drums, kegs, and pails	500
3469	Metal stampings, n.e.c.	250
3496	Miscellaneous fabricated wire products	250
3449	Miscellaneous metalwork	250
3463	Nonferrous forgings	250
3489	Ordnance and accessories, n.e.c.	250
34332	Plumbing fixture fittings and trim (brass goods)	500
3448	Prefabricated metal buildings and components	250
3451	Screw machine products	250

Census Classification Code	Industry or Class of Products	Employment Size Standard (number of employees)
3444	Sheet metal work	250
3484	Small arms	1,000
3482	Small ammunition	1,000
3493	Steel springs, except wire	500
3494	Valves and pipe fittings, except plumbers' brass goods	500
3495	Wire springs	250
Major Group 35: Machinery, Except Electrical:		
3563	Air and gas compressors	500
3585	Air conditioning and warm air heating equipment and commercial and industrial refrigeration equipment	750
3581	Automatic merchandising machines	250
3562	Ball and roller bearings	750
3564	Blowers and exhaust and ventilation fans	250
3574	Calculating and accounting machines, except electronic computing equipment	1,000
3592	Carburetors, pistons, piston rings, and valves	250
3582	Commercial laundry, dry cleaning, and pressing machines	250
3531	Construction machinery and equipment	750
3535	Conveyors and conveying equipment	250
3573	Electronic computing equipment	1,000
3534	Elevators and moving stairways	500
3523	Farm machinery and equipment	500
3551	Food products machinery	250
3524	Garden tractors and lawn and garden equipment	500
3569	General industrial machinery and equipment, n.e.c.	250
3536	Hoists, industrial cranes, and monorail systems	500
3565	Industrial patterns	250
3567	Industrial process furnaces and ovens	250
3537	Industrial trucks, tractors, trailers and stackers	750
3545	Machine tool accessories and measuring devices	250
35452	Precision measuring tools	500
3541	Machine tools, metal cutting types	500
3542	Machine tools, metal forming types	500
3599	Machinery, except electrical, n.e.c.	250
3586	Measuring and dispensing pumps	500
3568	Mechanical power transaction equipment, n.e.c.	500
3549	Metalworking machinery, n.e.c.	500
3532	Mining machinery and equipment except oil field machinery and equipment	500

Census Classification Code	Industry or Class of Products	Employment Size Standard (number of employees)
3579	Office machines, n.e.c.	500
3533	Oil field machinery and equipment	500
3554	Paper industries machinery	250
3546	Power driven handtools	500
3555	Printing trades machinery and equipment	500
3561	Pumps and pumping equipment	500
3547	Roofing mill machinery and equipment	500
3576	Scales and balances, except laboratory	250
3589	Service industry machines, n.e.c.	250
3544	Special dies and tools, die sets, jigs and fixtures, and industrial molds	250
3559	Special industry machinery, n.e.c.	250
3556	Speed changers, industrial high speed drives, and gears	500
3511	Steam, gas and hydraulic turbines and turbine generator set units	1,000
3552	Textile machinery	250
3572	Typewriters	1,000
3553	Woodworking machinery	250

Major Group 36: Electrical and Electronic Machinery, Equipment and Supplies

Census Classification Code	Industry or Class of Products	Employment Size Standard (number of employees)
3624	Carbon and graphite products	750
3672	Cathode ray television picture tubes	750
3646	Commercial, industrial, and institutional electric lighting fixtures	250
3678	Connectors for electronic applications	500
3643	Current-carrying wiring devices	500
3634	Electric housewares and fans	750
3641	Electric Lamps	1,000
3694	Electrical equipment for internal combustion engines	750
3629	Electrical industrial apparatus, n.e.c.	500
3699	Electrical machinery, equipment and supplies, n.e.c.	500
3675	Electronic capacitors	500
3677	Electronic coils, transformers, and other inductors	500
3679	Electronic components, n.e.c.	500
3639	Household appliances, n.e.c.	500
3631	Household cooking equipment	750
3633	Household laundry equipment	1,000
3632	Household refrigerators and home and farm freezers	1,000
3635	Household vacuum cleaners	750
3622	Industrial Controls	750
3648	Lighting equipment, n.e.c.	250
3621	Motors and generators	1,000
3644	Non-current-carrying wiring devices	500
3652	Phonograph records and prerecorded magnetic tape	750
3642	Power, distribution and specialty transformers	750
3692	Primary batteries, dry and wet	1,000
3651	Radio and television receiving type electron tubes, except cathode ray	1,000
3662	Radio and television transmitting signaling, and detection equipment and apparatus	750
3693	Radiographic X-ray fluoroscopic X-ray, therapeutic X-ray, and other X-ray apparatus and tubes; electro-medical and electro-therapeutic apparatus	
3645	Residential electric lighting fixtures	250
3676	Resistors, for electronic applications	500
3674	Semiconductors and related devices	500
3636	Sewing machines	750
3691	Storage batteries	500
3613	Switchgear and switchboard apparatus	750
3661	Telephone and telegraph apparatus	1,000
3673	Transmitting, industrial, and special purpose electron tubes	750
3647	Vehicular lighting equipment	250
3623	Welding apparatus, electric	250

Major Group 37: Transportation Equipment:

Census Classification Code	Industry or Class of Products	Employment Size Standard (number of employees)
3721	Aircraft	1,500
3724	Aircraft engines and engine parts	1,000
3728	Aircraft parts and auxiliary equipment, n.e.c.	1,000
3732	Boat building and repairing	250
3761	Guided missiles and space vehicles	250
3769	Guided missile and space vehicle parts and auxiliary equipment, n.e.c.	1,000
3764	Guided missile and space vehicle propulsion units and propulsion unit parts	1,000
3711	Motor vehicle and passenger car bodies	1,000
3714	Motor vehicle parts and accessories	500
3751	Motorcycles, bicycles and parts	500
3743	Railroad equipment	750
3731	Ship building and repairing	1,000
3795	Tanks and tank components	1,000
3799	Transportation equipment, n.e.c.	250
3792	Travel trailers and campers	250
3713	Truck and bus bodies	250
3715	Truck trailers	500

Major Group 38: Measuring, Analyzing and Controlling Instruments Photographic, Metal and Optical Goods; Watches and Clocks:

3822	Automatic controls for regulating residential and commercial environments and appliances	500
3843	Dental equipment and supplies	250
3811	Engineering, laboratory, scientific and research instruments and associated equipment	500
3823	Industrial instruments for measurement, display and control of process variables; and related products	500
3825	Instruments for measuring and testing of electricity and electrical signals	500
3829	Measuring and controlling devices, n.e.c.	500
3851	Opthalmic goods	250
3832	Optical instruments and lenses	250
3842	Orthopedic, prosthetic, and surgical appliances and supplies	250
3861	Photographic equipment and supplies	500
3841	Surgical and medical instruments and apparatus	250
3824	Totalizing fluid meters and counting devices	500
3873	Watches, clocks, clockwork operated devices, and parts	500

Major Group 39: Miscellaneous Manufacturing Industries:

3991	Brooms and brushes	250
3963	Buttons	250
3995	Burial Caskets	250
3955	Carbon paper and inked ribbon	250
3961	Costume jewelry and costume novelties, except precious metals	250
3942	Dolls	250
3962	Feathers, plumes, and artificial trees and flowers	250
3944	Games, toys and children's vehicles except dolls and bicycles	250
3915	Jeweler's findings and materials and lapidiary work	250
3911	Jewelry, precious metal	250
3952	Lead pencils, crayons, and artists' materials	250
3996	Linoleum, asphalted felt base, and other hard surface floor coverings, n.e.c.	750
3999	Manufacturing industries, n.e.c.	250
39993	Matches	500
3963	Marking devices	250
3931	Musical instruments	250
3964	Needles, pins, hooks, and eyes, and similar notions	250
3951	Pens, mechanical pencils, and parts	500
3993	Signs and advertising displays	250
3914	Silverware, plated ware, and stainless steelware	500
3949	Sporting athletic goods, n.e.c.	250

SBA Requirements

A regulated firm is eligible to apply for a Federal Water Pollution Control loan only if it meets certain requirements of the Small Business Administration and the Environmental Protection Agency.

The Small Business Administration considers a business to be eligible for a pollution control loan application if:

- the firm meets small business size standards,
- the business is not new
- the firm meets certain industry classification requirements
- the business demonstrates that regulatory requirements will cause the firm serious economic injury
- the business has received certification from the Environmental Protection Agency that the proposed pollution abatement measure(s) are necessary and adequate to comply with regulatory requirements imposed on the firm.

TO APPLY FOR A LOAN - STEP-BY-STEP PROCEDURE

1. Prepare a current financial statement (balance sheet) listing all assets and all liabilities of the business - do not include personal items.

2. Have an earning (profit and loss) statement for the previous full year and for the current period to the date of the balance sheet.

3. Prepare a current personal financial statement of the owner, or each partner or stockholder owning 20 percent or more of the corporate stock in business.

4. List collateral to be offered as security for the loan, with your estimate of the present market value of each item.

5. State amount of loan requested and explain exact purposes for which it will be used.

6. See your banker. Ask for a direct loan and if declined, ask the bank to make loan under SBA's loan guaranty plan or to participate with SBA in a loan. If the bank is interested in an SBA guaranty or participation loan, ask the banker to contact SBA for discussion of your application.

7. Visit SBA office for direct loan for economic injury loan for water pollution control, apply after you received EPA or other official notification and have consulted with your engineer and devised an abatement plan.

In addition to the SBA loan program their are various other government agencies that have programs which may be beneficial to businesses seeking help for their pollution control abatement needs.

The Economic Development Administration has direct loans or loan guarantees with interest rates below market. The Farmers Home Administration also has various loan and grant programs.

SBA Guaranteed Pollution Control Revenue Bonds

Public Law 94-305 authorized SBA to guarantee the payments under qualified contracts entered into by existing small business concerns which are, or are likely to be, at an operational or financing disadvantage with other businesses for the purpose of acquiring pollution control facilities. The statute specifically provides that financing of the pollution control facilities can be obtained through the use of industrial revenue bonds issued by a state or municipality.

The purpose of using tax exempt industrial revenue bond financing for pollution control facilities is to obtain the most advantageous interest rate and repayment terms possible.

Revenue bond financing is, and has been, extensively utilized by large businesses for their financing of pollution control facilities. Large businesses which are dominant in their industry, are generally recognized nationally and/or internationally and they usually have a very wide market available, including the bond market, for their financing needs. Small businesses on the other hand, because they are primarily local or regional operations and account for only a very small percentage of their industry's output, do not generally have wide sources of financing available. The Department of Treasury estimates that in 1978, 3.1 billion worth of industrial bonds for pollution control were issued and by 1979 the figure is expected to rise to 3.3 billion. To implement Public Law 94-305, SBA is cooperating with commercial banks, state authorities, and bond underwriters to make long-term, low interest financing available to well established larger small businesses through tax-exempt revenue bonds. This is essentially the same way large corporations obtain financing for their pollution facilities.

1. Public entity issues tax exempt revenue bonds on which repayment is based solely on the credit of the business.

2. Public entity is the nominal owner of the property.

3. Property is conveyed to the business under a lease, lease-purchase installment sale, etc.

4. The business may obtain additional tax advantages such as the investment tax credit and accelerated depreciation.

The need for the program is to put a smaller firm on an equal footing with the giant firms. The program may also allow smaller firms to combine into one package their requirement and issue the bonds collectively.

To qualify for this program a small business must be one which together with its affiliates is independently owned and operated, is not dominant in its field of operation and has less than nine million dollars in annual revenues.

The company must have a net worth less than 4 million dollars and an average net income over the past two years less than $400,000.

The company had to be in existence at least 5 years of which 3 out of the last 5 years were profitable. The most important criteria, however, is that the company has sufficient cash flow to pay off the debt over a twenty year period.

The applicant must provide evidence of the need for the pollution control facility (from State or Federal Agency).

The company may qualify as a small business concern under 121.3-10 (no. of employees of specific industry group.)

Applicants for guaranteed financing through the authority should have qualified sponsors (their bank or other financial organization). The sponsor must provide the authority and SBA with a certificate that applicant is creditworthy, and is at a financing or operational disadvantage in the long term, tax exempt credit makers.

To be eligible the project must be new, and the application must be processed and accepted before construction begins.

The repayment period for the pollution control financing is 25 years and will generally be tied to the expected useful life of the facility.

The required financing should not exceed 4 million dollars. Generally included are all costs connected with construction and/or installation of the facility.

What is the process?

A small business initially requests a loan from a state or local authority empowered to issue the bonds.

In most states it is the state economic development agency or business development agency. In other areas, bonds are issued directly by municipalities.

The authority in turn requests that the SBA guarantee the loan. The SBA, after reviewing the applicants' business qualifications under program guidelines, agrees to guarantee the loan and reports to the authority. When the authority has several businesses with SBA approval it can package a bond issue of marketable size. The issue is marketed through an underwriter and the proceeds from the issue are made to the businesses.

The loan funds are deposited with an appointed trustee. The businessman can use the proceeds, over a three year period, to finance construction and equipment required to meet environmental control standards, costs of site preparation, and all expenses necessary to begin and supervise construction, including legal and engineering costs. These funds may also be used to pay bond issuance expenses, application fees, establish a

reserve fund and refinance existing debt for a pollution control facility. They may not be used to replenish working capital. Funds are dispersed by the trustee upon receipt of invoices for any of the approved uses.

How available is the financing?

The market for SBA guaranteed Industrial Pollution Control Bonds is strong. California, Illinois, and Alabama have already issued bonds. Six or eight other states have the machinery in place, and by the end of this year at least half the states will be prepared to provide such financing.

It is up to the businessman to seek out the issuing authority in his state.

For further information on any of the financial assistance programs call me at (202-755-3624) or write to me at 401 M St. S. W., mail code WH-586, Washington, D. C. 20460

SUMMARY OF EVENING SESSION

Purpose of Evening Session

To concentrate on frank interchanges between attendees, consultants and EPA officials on the metal finishing industry's needs and problems in pollution control technology.

Evening Session Panel Members:

Moderator: **Kenneth Coulter,** AES Environmental Committee

Panelists: **Dr. E. E. Berkau,** Dir., EPA Industrial Pollution Control Division, Industrial Environmental Research Lab.

Robert B. Schaffer, Dir., EPA Effluent Guidelines Div., Washington, DC

Nancy J. Hutzel, Program Analyst, EPA Permits Div., Office of Water Enforcement, Washington, DC

Gary McKee, Supervisory Chemist, EPA Environmental Monitoring & Support Lab., Cincinnati, OH

John Dickenson, Coordinator, Solid Waste Section, Region IV, EPA, Atlanta, GA

Simon P. Gary, AES First Vice President, Scientific Control Labs., Inc.

Richard W. Crain, AES Environmental Committee, Industrial Filter and Pump Mfg. Co.

Dr. Clarency Roy, AES Environmental Committee, Aqualogic Inc.

Bud Weber, Genessee Valley Metal Finishing Co., Inc.

SUMMARY OF DISCUSSION POINTS RAISED DURING EVENING SESSION

The vast majority of the comments and questions raised during the evening session dealt with the regulations affecting the electroplating industry, the need to communicate these regulations to the users, and the need for RD&D in sludge characterization and centralized treatment. Specifically:

- There were many questions to Robert Schaffer relating to which regulations affected the electroplating industry and when they became effective. Nancy Hutzel was asked how the pretreatment requirements affected the electroplating industry, especially the requirements of 40CFR303. This section requires reporting within 180 days after the publication of the general pretreatment regulations on the status of meeting pretreatment regulations. It was obvious from the comments that most of the electroplaters present were not aware of the reporting requirement, and those who were aware were not sure of the status of the proposed regulations for electroplating. Mr. Schaffer stated that he would check with EPA's Office of General Council to determine the status of the regulations.

- There was a question as to which has priority - state and local regulations, or federal regulations. The answer was that nothing precludes a state or local agency from setting any regulation that they wish, but that the federal overrides state and local regulations if the federal regulation is more stringent.

- One conference attendee pointed out that the preamble to the Resource Conservation and Recovery Regulations mentions that inadequate data are available to set regulations. He asked what EPA was doing in this regard. Dr. Eugene Berkau reported that the EPA/AES grant on sludge characterization had been awarded and work to provide data would be underway shortly.

- Several electroplaters expressed that the cadmium problem could be solved if military specifications did not require the use of cadmium in electroplating. Simon Gary expressed a belief that cadmium was advantageous for some uses.

- A great deal of support for the centralized treatment research was evidenced. Timing of this project was also emphasized in that electroplaters need answers soon if the option is to be viable. Dr. Berkau explained that the phased approach of screening regions first, rather than going ahead with the demonstration, is necessary because it is important that the demonstration be successful and representative of a wide range of situations in the United States.

- A potential problem with the pretreatment regulation was highlighted by questions as to how changing POTW removal allowances are handled. Electroplating representatives explained that if a system were designed for a large removal allowance, a change in that removal allowance could result in redesign of the system.

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- There were a number of questions on the legal ramifications of sludge handling and disposal. A great deal of concern on the electroplater's part was evident as to possible long-term liabilities from the waste material generated. It was explained that this issue would be dealt with on a case-by-case basis by local courts.

- There was a question as to when a source becomes a new source. Mr. Schaffer explained that if construction is initiated after proposal and the regulation is promulgated within 120 days after proposal, it is a new source. In the case of electroplaters, there will not be any new sources until the regulation is promulgated, because it has been more than 120 days since proposal.

- A question was raised as to how a person petitions to get a pollutant removed from the priority pollutant list. Mr. Schaffer explained that the proper procedure was to send a letter to the Effluent Guidelines Division requesting such a deletion. He mentioned that several of such requests have been received.

- A representative of one of the trade magazines, along with many electroplaters in the audience, expressed the need for better communication of regulations from EPA to the affected industries. They explained that most electroplaters do not read the Federal Register and when they do, they have difficulty understanding the legal language.

- Concerns were expressed as to the need for the Office of Solid Waste and the Effluent Guidelines Division to work more closely together.

- There were only a few technical questions. Clarence Roy discussed types of treatment for copper and nickel complexes and the technology and shortcomings of breakpoint chlorination.

Water Recycling and Nickel Recovery Using Ion Exchange

Kenneth Price (Oldsmobile) & Charles Novotny (Industrial)*

In 1972 Oldsmobile installed two ion exchange systems supplied by Industrial Filter & Pump Mfg. Co. The exchange systems were designed to treat nickel rinse water from the bumper plating lines at Plants #1 and #3.

The treatment systems were designed to accomplish three purposes: (1) Reduction of nickel metal in the plant effluent discharged to the City of Lansing, (2) Recovery of nickel metal, (3) Recovery of the rinse water itself.

General Process Description

The nickel rinse water from the spray rinse following the final nickel plating step is collected in a sump and pumped to a 10,000 gallon filter supply tank. The transfer pumps operate automatically and are controlled by level controls in the sump tank.

From the filter supply tank, the water is pumped through a filter to remove Dur-Ni solids present in the final plating step before rinsing. A coagulant is added to aid in the filtration.

The filtrate then passes through one of two, three-bed ion exchange trains. The first column is a cation exchanger using Dowex HCR-W strong acid resin. This column removes the nickel and other cations present in the water. The water continues on through a weak base exchanger containing Dow WGR resin and a strong base exchanger containing Dow SBR resin.

This combination of weak base exchange followed by strong base exchange takes advantage of the high capacity and efficiency of weak base resin regeneration to remove most of the anions and the ability of the strong base resin to remove silicates and borates for a final "polish."

The solution emerging from the strong base exchanger is high quality demineralized water. This is stored in a 5000 gallon D. I. water tank and recycled back into the plating process as the nickel spray rinse. Make-up water is added to the storage tank as required. This water is also deionized.

When one train becomes exhausted, the other train is put on stream and the exhausted train is regenerated. The cation column is regenerated with sulfuric acid. A quadruple reuse of acid is employed to reduce the amount of excess acidity in the spent regenerant.

The anion exchangers are regenerated in series. Fresh sodium hydroxide solution is pumped into the strong base exchanger and then into the weak base exchanger. There is enough free sodium hydroxide left after passing through the strong base column to regenerate the weak base column.

The recovered nickel sulfate solution, at about 5.0 - 5.5 oz/gallon nickel metal, is further concentrated to 10.0 - 11.0 oz/gallon nickel metal using an atmospheric evaporator. The concentrated solution is sold for reprocessing.

During periods of downtime on the plating process - weekends, breakdown, etc. - a level control in the filter supply tank diverts the water from the strong base exchanger back to the filter supply tank. This permits a constant "head" on the filter and prevents potential "souring" of water that would stay in the exchange columns if flow were stopped.

Process Specifications

An ion exchange train is considered exhausted when the water emerging from the strong base exchanger has a resistance of 20,000 ohms @ 60° F. A freshly regenerated train is considered ready for service at the same point.

The resin volumes for the exchange columns are: Plant #3: Cation 100 ft.³, weak base 135 ft.³, and strong base 50 ft.³. At Plant #1: Cation 65 ft.³, weak base 85 ft.³, and strong base 30 ft.³. The size differences between plants are due to the fact that the plating capacity at Plant #1 is less than Plant #3. The rinse rate is also lower at Plant #1.

The cycle time for one three-bed system is approximately 60 hours at each plant. Since each cubic foot of cation resin has an estimated capacity of 2.0 - 2.4 pounds of nickel, each cycle removes 200 - 240 pounds of nickel at Plant #3 and 130 - 155 pounds of nickel at Plant #1.

The cation resin at Plant #3 is regenerated with 500 gallons of 20% sulfuric acid (950 pounds).

The anions resins are regenerated with 510 gallons of 10% caustic, (950 pounds of 50% NaOH).

Correspondingly, for Plant #1, the cation resin requires 350 gallons of 20% sulfuric acid (665 pounds); the anion resins use 300 gallons of 10% caustic (550

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*Kenneth Price
Oldsmobile Div., GMC, Lancing, MI

Charles J. Novotny
Industrial Filter & Pump Mfg. Co., Cicero, IL

pounds of 50% NaOH). The table below summarizes these data:

	Plant #3	Plant #1
Rinse Flow	100 gpm	60 gpm
Cation Resin	100 ft.³ DOW-HCR-W	65 ft.³ DOW-HCR-W
Weak Base Resin	135 ft.³ DOW-WGR	85 ft.³ DOW-WGR
Strong Base Resin	50 ft.³ DOW-SBR	30 ft.³ DOW-SBR
Cation Regenerant	950 lbs. H₂SO₄	665 lbs. H₂SO₄
Anion Regenerant	950 lbs. 50% NaOH	550 lbs. 50% NaOH
Cycle Time	60 hours	60 hours
Ni conc. in Feed	40 - 60 PPM	40 - 60 PPM

Regeneration

Regeneration of a train is initiated by the attendant simply by energizing the first step in an automatically sequenced series of regeneration steps. The indexing from one step to another is then controlled by a timer or level control. Each step may be controlled by a manual advance cycle button if an extended time on a given step is desired.

The quadruple use of acid is accomplished by using a series of five tanks. The last tank is the final used acid and the first is the fresh acid.

During regeneration, the thrice used acid is pumped into the exchanger and displaced by twice used acid; the twice used acid is displaced by once used acid; the once used acid by fresh acid; and the fresh acid by water. Thus the solution is displaced down the line of tanks until the final concentrated solution is obtained.

The caustic regenerant is pumped into the strong base exchanger and on into the weak base exchanger. The regenerant is then displaced from the strong base through the weak base with decationized water and the columns reused in series.

Finally the entire three-bed train is rinsed - usually an hour to one and one half hours - until a water quality of 20,000 ohms is reached.

Problems

The original intent of the recovery system was to recycle the water and reuse the nickel sulfate solution back in the plating tanks.

In order to do this, a number of conditions needed to be met:

1. The pH of the solution to be 3.0 - 3.5, 2. Only minute quantities of contaminating metals could be present, 3. A low level of sodium ion - 2000 ppm or below - had to be achieved.

To adjust the final used acid to an acceptable level, the process was to employ a single weak base exchange column containing DOW-WGR resin.

The solution from the cation regeneration was to be pumped through this column where the excess acidity was to be removed. The weak anion resin was expected to be capable of removing this excess acid without splitting the neutral nickel sulfate salts.

This was never achieved. The metal precipitated in the column causing fouling. Partial regeneration to reduce

column capacity was attempted but no improvement was noted. The problem appeared to be due to the fact that although the volume of resin available has the capability of removing the excess acidity from a batch of solution, only a small amount of solution contacts the resin at a given time. The pH of the environment precipitates the nickel that eventually plugs the column and prevents the continued flow of acid solution. The precipitated metal can not be redissolved by incoming low pH solution.

Efforts to utilize ion exchange to adjust the pH of the solution were abandoned and nickel carbonate was used to achieve the desired pH.

A low level of sodium ion was required because the solution was to be added to the semi-bright nickel plating tank. Dragout from one plating tank into the other meant that the first nickel plating step needed the vast majority of nickel salt additions. Sodium ion is known to have a limiting effect on current in semi-bright nickel.

Since the amount of sodium ion in Dur-Ni plating bath is higher in proportion to the nickel metal than is acceptable in semi-bright, immediate regeneration of a cation column after exhaustion would have resulted in excess sodium levels in the recovered solution.

To remove unwanted sodium ion from the cation column, a deplacement step was used.

Displacement takes advantage of the fact that although a cation resin will remove all cations from a solution, it will hang on to some much more tightly than others.

When a column becomes exhausted, nearly all the sites on the column are occupied by a cation. If a mixture of cations in solution is allowed to pass through this exhausted column the resin will continue to exchange. The resin will exchange a weakly held cation for a more strongly held cation.

In this case, when nickel rinse water is passed through an exhausted column, the column will exchange a nickel ion in the solution for a sodium ion on the resin. Thus the sodium ion is displaced from the resin into the solution. The sodium laden rinse water is permitted to pass from the cation column into the plant effluent.

The displacement is allowed to continue until enough sodium has been displaced that the regenerant solution is low enough to be used in the plating bath.

The time required to displace sodium was expected to be 30 min. During this period, the nickel rinse water flowed into the cation column and into the plant effluent. Thus, no water was recycled while sodium was being displaced.

It was found that 30 min. did not allow sufficient time to displace sodium. In order to achieve acceptable levels of sodium ion a four to six hour displacement period was required.

This long period of displacement depleated the supply of D.I. water. The original process used soft water at Plant #3 and city water at Plant #1 as make-up. The addition of large amounts of city water at Plant #1 elevated calcium levels in the recovered solution. Calcium salts precipitated in the plating tank on the air

agitation system and eventually forced us to discontinue the reuse of the solution in the plating tanks.

At Plant #3 the soft water make-up added enough sodium ion that the displacement step did not reduce sodium levels enough to allow use of the solution.

The long displacement time was due to two factors:

One was that changes in the configuration of the bumpers reduced the nickel concentration in the incoming rinse water by 50 - 60 percent. This meant less metal was available to displace the sodium and displacement time was increased.

The second reason was that the use of city and soft water as make-up introduced additional sodium into the system which also lengthened displacement time. Oldsmobile felt that D. I. water make-up was not necessary even though it was recommended by the equipment manufacturer.

It is now felt that if deionized (or at least decationized) water were used for make-up, the recovered nickel would be reuseable directly into the plating tanks. First, there would be few cations present other than nickel and the displacement of sodium step would be much shorter.

Next, the recovery ion exchange system cycles would be lengthened by the reduced load. Overall operating expensed would not be increased by addition of make-up water demineralizers since the mineral content of the make up is now being removed by the recovery system. In fact, overall economics would be improved.

Summary

Although the ion exchange processes at Oldsmobile did not fully achieve all the objectives hoped for, it still recycles a combined 50 million gallons of water and recovers about 30,000 lbs. of nickel metal annually.

In addition, significant reductions of nickel metal in plant effluent has been observed.

Oldsmobile is also able to rinse following a Dur-Ni plating step with only one rinse tank. In many cases, several rinse steps are used   reclaim, cold water, hot water - to conserve water and reduce nickel dragout.

Using one tank instead of two or three is accomplished because a high volume of water may be employed without wasting water. The metal, in very small concentration, can also be recovered.

This can be an advantage if space requirements are a consideration when a new installation or modification of old equipment is contemplated.

Resin attrition rates indicate that a constant replacement of resin at high expense is not a factor for consideration in this type of ion exchange application.

Periodic checks of the resins show the following losses in total resin capacity per year.

Cation Resin	2% - 3%
Weak Base Resin	Under 1%
Strong Base Resin	3% - 4%

Normal cleaning of resins is limited to an occasional (once or twice per year) soaking of the resins with warm (140° F.) inhibited hydrochloric acid.

Most waste treatment processes will not be self-supporting. The ion exchange process described is not self supporting since not all of the operating costs are recovered. However, recycling does eliminate much of the cost associated with methods that generate a solid waste that must be disposed.

Recovery and recycling using ion exchange has wide application in the electroplating industry. Its use should be given careful consideration when waste treatment systems are being designed.

Field Demonstration of Closed-Loop Recovery Of Zinc Cyanide Rinsewater Using Reverse Osmosis and Evaporation

Kenneth J. McNulty & John W. Kubarewicz*

ABSTRACT

A field test was conducted to demonstrate closed-loop recovery of zinc cyanide rinsewater at a job shop plating facility. Since the zinc cyanide bath operates at room temperature with very little evaporation from the bath, reverse osmosis (RO) treatment of the rinsewater must be supplemented by evaporation in order to achieve the volume reduction necessary for return of a concentrate to the plating bath. The permeate from the RO unit was recycled to the first rinse after plating while the distillate from the evaporator was recycled to the second rinse after plating. Continuous, unattended operation of this system was demonstrated with no adverse effects on plating quality.

Spiral-wound PA-300 membrane modules were used in the RO unit. Periodic tests were conducted throughout the demonstration to characterize membrane performance under standard conditions. These tests indicated a gradual loss in membrane flux and rejection. After 3,000 hours of exposure to the rinsewater, the membranes were cleaned by flushing with a cleaning solution. The cleaning resulted in nearly complete restoration of flux and rejection. The gradual loss in membrane performance is thus attributable to fouling of the membrane by particulates in the rinsewater. Such fouling can be reduced by better pre-filtration and reversed by periodic cleaning.

The economics of the combined RO evaporation system were assessed for a system designed to provide rinsing equivalent to the present two-stage counter-current rinse at the demonstration site. The analysis showed that the total operating cost (including amortization) was somewhat less for the combined RO evaporation system than for evaporation alone. The minimum cost occurred for 90% water recovery in the RO system. However credits for rinsewater recovery were insufficient to completely off-set the total operating cost of the recovery system.

INTRODUCTION

Wastewater treatment technologies for the electroplating industry can be broadly classified as end-of-pipe destruction processes or in-plant recovery processes. The end-of-pipe destruction processes treat a total shop effluent to remove a mixture of heavy metals. At present it is neither technically nor economically feasible to recover and recycle metals from the end-of-pipe processes (1). On the other hand, in-plant recovery processes treat rinsewater from a specific plating bath (or other operation) making it possible to recover and return the heavy metals to the plating bath.

Because of the inherent disadvantage of end-of-pipe treatment—loss of valuable plating chemicals, cost of treatment chemicals, cost of sludge disposal—increasing attention has been focused on closed-loop recovery methods. In many cases, the economics of closed-loop recovery have been very favorable resulting in rapid payback on the capital investment for recovery equipment (2).

Aside from a few applications in which closed-loop recovery can be achieved by countercurrent rinsing alone, some technique must be used to remove the dissolved plating chemicals from the rinsewater. Although other techniques are under development, evaporation, reverse osmosis (RO), and ion exchange are the most commonly used processes for rinsewater recovery (1, 3). Each of these techniques has particular advantages and disadvantages, and the best technique or combination of techniques will depend on factors specific to each application.

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A number of advantages can be cited for the use of RO in rinsewater recovery. These include low capital cost, low energy and operating costs, and minimal space requirements. However, there are also some limitations. The two major limitations for RO are:

1. The membrane modules deteriorate with time and require periodic replacement. The rate of deterioration depends on the type of membrane, the rinsewater pH and temperature, and the concentration of other reactants in the rinsewater such as oxidants.

2. Reverse osmosis cannot produce a highly concentrated stream for recycle to the plating bath. Thus for ambient temperature baths, RO must be supplemented with some other concentration technique, such as evaporation, in order to close the loop.

To date, RO has been applied primarily to the recovery of nickel rinsewaters. For nickel, the rinsewaters are relatively mild in pH (4-6) resulting in acceptable life for the conventional commercial membranes (cellulose acetate and aromatic polyamide). In addition, nickel baths operate at elevated temperatures where substantial evaporation occurs, and closed-loop operation can be achieved with RO alone.

Several programs, jointly sponsored by EPA and AES, have been conducted to evaluate the applicability of RO to plating baths other than nickel (4, 5, 6). Laboratory tests were conducted with a variety of newly developed membranes and rinsewaters with extreme pH levels (6). These tests indicated that of the membranes tested, the PA-300 was superior to the other membranes for treatment of copper cyanide, zinc cyanide, and chromic acid rinsewaters. The PA-300 membrane has since been commercialized (currently designated TFC-PA; manufactured by Fluid Systems Division of UOP) and is available in a spiral-wound modular configuration.

A field test was undertaken to evaluate the PA-300 membrane module for recovery of zinc cyanide rinsewater under realistic conditions. Zinc cyanide was selected because of the large volume of zinc cyanide plating done by the industry and because the high pH of the rinsewaters would provide a "worst case" test of the membrane for resistance to alkaline conditions. Since the zinc cyanide bath operates at room temperature, it was necessary to use an evaporator to supplement RO treatment and achieve the level of concentration necessary for closed-loop operation. This paper presents and discusses the results of this field test.

METHODS AND MATERIALS

A mobile RO test system was leased from Abcor, Inc. and an evaporator was leased from Wastesaver Corporation for the duration of the field test. These two units were installed on an automatic rack, zinc cyanide plating line at New England Plating Co. in Worcester, Massachusetts. The overall schematic of the installation is shown in Figure 1. Feed to the RO system was withdrawn from Rinse Tank No. 1 and separated by the
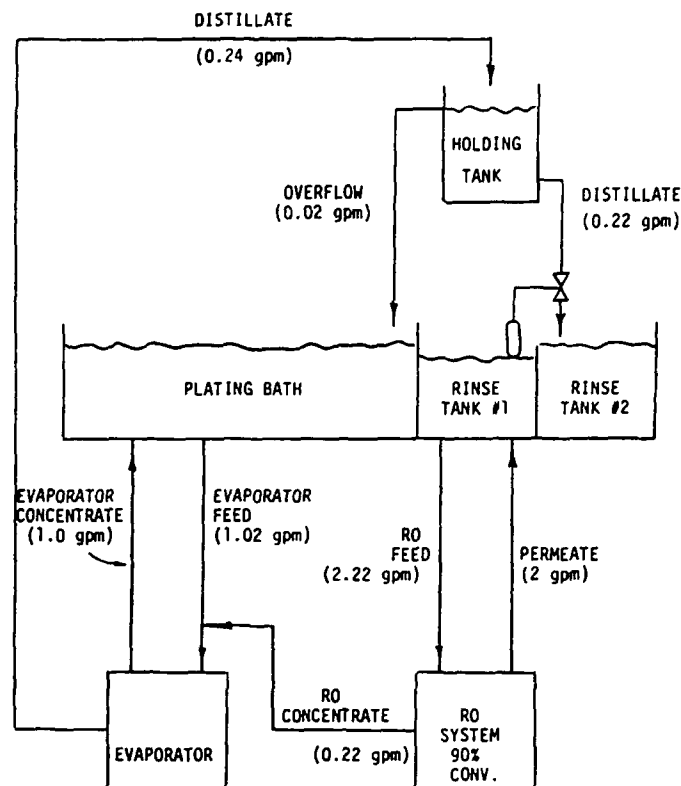
Fig. 1—Overall Schematic of RO/Evaporator Operation.

RO system into a permeate stream and a concentrate stream. For purposes of design, it was assumed that the RO system would produce about 2 gpm of permeate and would operate at 90% conversion. (Conversion is defined as the ratio of permeate flow to feed flow.) Thus the RO system would be fed at the rate of 2.22 gpm and would produce concentrate at the rate of 0.22 gpm. The permeate was returned to Rinse Tank No. 1 and the concentrate was fed to the evaporator.

Since dragin and dragout were essentially identical for the plating bath and the rate of evaporation was negligible, there was no room in the plating bath for a concentrate stream. If the evaporator were fed only RO concentrate, it would have to evaporate it to dryness in order to prevent eventual overflow of the bath. In order to prevent precipitation of plating chemicals in the evaporator a 1 gpm purge stream was circulated from the plating bath through the evaporator and carried the plating salts introduced with the RO concentrate back to the plating bath. That is, the evaporator concentrate was higher in concentration than the plating bath by the amount added by the RO concentrate. The distillate from the evaporator was collected in a holding tank and added at a controlled rate to Rinse Tank No. 2. A float valve operating off the level in Rinse Tank No. 1 insured that the rate of RO concentrate production was exactly balanced by the rate of distillate returned to Rinse Tank No. 2. A slight excess of distillate was produced to insure that the holding tank would always remain full; and the excess was permitted to overflow into the plating bath (0.02 gpm). The steam rate was cut back to minimize overflow from the holding tank.
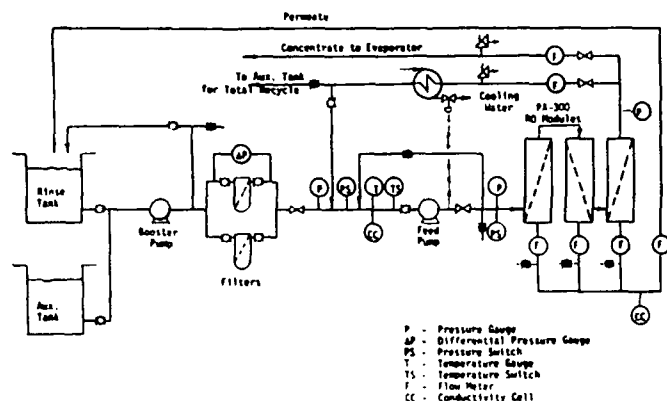
Fig. 2—Flow Schematic for RO Demonstration System.

Fig. 3—Flow Schematic for Evaporator.

A flow schematic of the RO system is shown in Figure 2. Feed from the first rinse tank was withdrawn by a booster pump and passed through two cartridge filters in parallel. Both 1-μ and 20-μ filters were used at different times during the field test. Excess flow from the booster pump was returned to the rinse tank. After pre-filtration, the feed was pressurized to 700 psi with multi-stage centrifugal feed pump and passed through three 4-inch diameter, spiral-wound, PA-300 modules arranged in series. Most of the concentrate from the third module was recycled to the suction of the feed pump in order to maintain the required feed flow rate through the modules. A heat exchanger in the recirculation loop removed heat generated by the energy input of the pumps. A small flow of concentrate from the third module was fed to the evaporator (see Figure 1), and the permeate from the three modules was combined and returned to the first rinse tank. The instrumentation and controls for the RO system are shown in Figure 2.

In order to characterize membrane performance with a standard feed solution, the RO system was periodically operated in a total recycle mode using the auxiliary feed tank. For this mode of operation, the booster pump recycle line was closed off, the concentrate line to the evaporator was opened, and the permeate was returned to the auxiliary tank rather than the rinse tank. The standard solution (generally a portion of plating bath diluted to 10% by volume of original bath strength) was charged to the auxiliary tank and the system was operated with total recycle until steady state was achieved. At steady state, the permeate flow rate for each module was measured, and samples of the feed and permeate from each module were obtained for analysis.

Typical operating conditions for both closed-loop and total recycle were:

Feed Pressure	700 psi
Recirculation Flow Rate	10 gpm
Temperature	70 - 90° F
Concentrate Flow Rate	0.2 gpm (closed-loop only)

The flow schematic for the evaporator is shown in Figure 3. Steam was fed through a pressure reducing valve to a tube bundle submerged in the boiler section of the evaporator, and steam condensate was returned to
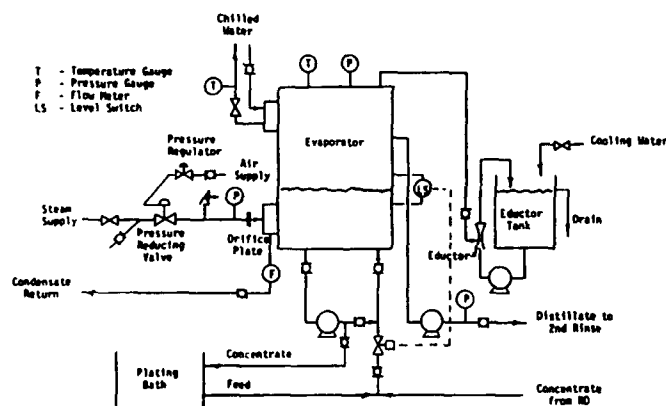
the plant boiler. For most installations, a cooling tower is used to cool the water which is recirculated through the condenser section of the evaporator. However, for this installation it was more convenient to use recirculated chilled water since it was readily available at the installation site and the chiller had sufficient excess capacity. The evaporator was maintained under vacuum by circulating water through an eductor. Cooling water was added to the eductor tank to remove the energy input of the eductor circulation pump. Feed to the evaporator was controlled by a level switch (LS) and solenoid valve. Upon low level signal, the solenoid valve opened and feed was drawn by vacuum into the evaporator. The distillate from evaporation of the feed condensed, was collected in a tray below the condenser, and was continuously pumped back to the second rinse after plating (see Figure 1). The concentrate from the boiler section of the evaporator was continuously pumped back to the plating bath.

Typical operating conditions for the evaporator were:

Vacuum	26 - 27 in. Hg
Temperature	100 - 110° F
Steam Pressure	< 5 psi
Concentrate Flow Rate	1 gpm

During the field test, the RO modules were cleaned using a cleaning sequence recommended by the membrane manufacturer. The modules were first flushed with 50 gal of water to remove the plating chemicals. A 0.1% by volume solution of Triton X-100, a non-ionic surfactant, was prepared and recirculated through the modules at a pressure of 700 psi, a flow rate of 10 gpm, and a temperature of 120° F for 45 minutes. After flushing with another 50 gallons of water, 2% citric acid solution was prepared and adjusted to pH 3.0 with ammonium hydroxide. This solution was recirculated through the modules at the same conditions and for the same time as the Triton X-100. Following the citric acid cleaning the system was again flushed with water and returned to treatment of zinc cyanide rinsewater. Since the PA-300 membrane is rapidly degraded by chlorine, all water used for flushing and preparing cleaning solutions was dechlorinated by the addition of sodium sulfite.

Samples collected during the field test were analyzed for zinc (atomic absorption), free cyanide (selective ion electrode), total solids (gravimetric) (determination of residue), conductivity (conductivity bridge), and pH (electrode).

The nominal composition of the plating bath was:

Zn (as metal)	20.000 mg/l	2.7 oz/gal
CN (as NaCN)	60.000 mg/l	8.0 oz/gal
Caustic	75.000 mg/l	10.0 oz/gal
Brightener		
(700 Special)	4 ml/l	4 gal/1000 gal

In addition to these compounds, polysulfide was regularly added to the bath for purification, and the bath also contained a large quantity of carbonates. The total solids concentration of the bath was in the vicinity of 350,000 mg/l (35% by weight).

RESULTS AND DISCUSSION

Field activities covered the months of June through December of 1978. During this time, the system was operated primarily in the closed-loop mode shown in Figure 1. However, closed-loop operation was periodically interrupted to conduct total recycle tests on the RO system. The performance of RO modules is generally assessed in terms of the module flux (rate of permeate production per unit membrane area) given in gallons per ft^2 per day (gfd) and the rejection (defined for a particular dissolved species as one minus the ratio of permeate to feed concentrations) given in percent. Since both flux and rejection depend on feed concentration, it is necessary to conduct RO performance tests at a fixed feed concentration in order to be able to accurately interpret trends in the flux and rejection data. During closed-loop operation the feed concentration to the RO system can vary considerably (depending on the parts being plated and their dragout); hence total recycle tests at a fixed feed concentration (10% of bath strength) were periodically conducted to accurately assess trends in the RO system performance. System performance was monitored less rigorously during operation in the closed-loop mode.

The total operating time for the field demonstration (time during which permeate was being produced) was approximately 1000 hours. The total exposure time of the modules to the rinsewater, however, was about 4,200 hours. The longer exposure time reflects the system down-time during which the modules were sitting in contact with the concentrated zinc cyanide rinsewater. Various factors contributed to the system down-time, including: electro-mechanical failure of various system components, high or low alarm shut-down of the system, weekends and holidays. The total exposure time is probably more significant than operating time in controlling the degree to which the modules are attacked chemically by constituents in the rinsewater (e.g., caustic). On the other hand, operating time is more significant in controlling the degree to which the modules become fouled with particulates in the feed. Correlations presented below are based on exposure time. However, the operating time was reasonably evenly spread over the test program, and correlations on an operating-time basis would be similar.

Closed-Loop Operation

The RO/evaporator system was designed to operate continuously, with no operator attention, between start-up Monday morning and shut-down Friday afternoon. However, during most of the field test program, various electro-mechanical and other problems occurred which prevented unattended week-long operation. Each failure generally resulted in several days down time because of the logistics of getting project personnel to the field site, diagnosing the problem, and implementing remedial action. Eventually these problems were solved and week-long unattended operation was demonstrated.

During demonstration of the closed-loop system, no adverse effects were noted on the quality of the plated parts. However, the rinse tanks after zinc plating were followed by an acid dip, a flowing rinse, and other surface finishing steps before the parts were finally inspected. Therefore the degree of rinsing following zinc cyanide plating was probably not of critical importance to quality control.

Both the RO system and evaporator were under-designed as a direct replacement for the two-stage countercurrent rinse at a nominal rinsewater flow rate of 2 gpm (see "Economics" below). The system design reflected limitations imposed on program costs, availability of PA-300 modules at the time the system was fabricated, and lack of design data for the zinc cyanide application. Nevertheless, the system was of sufficient size to obtain meaningful design and economic data.

RO performance during closed-loop operation was monitored by measuring the productivity of each module (rate of permeate production) and by monitoring the conductivity of the combined RO permeate. In general, the productivity during closed-loop operation was similar (but slightly higher) than the productivity during the total recycle tests (see discussion below). The conductivity of the combined permeate generally ranged between 2,000 and 4,500 μ-mhos/cm. This is equivalent to a total solids concentration of approximately 1,000 to 2,000 mg/l.

The evaporator was operated at about one-half of its rated capacity (15 gal per hour vs. a capacity of 25 gph). Samples of distillate and evaporator concentrate were obtained and analyzed for zinc, free cyanide, total solids, conductivity and pH. The results of these analyses are presented in Table I. During closed-loop operation at the time the samples were taken, a stream of about 1.5 gpm from the bath was circulated through the evaporator and back to the bath in order to prevent precipitation of plating salts in the evaporator. Thus, the evaporator was operating on a feed very similar in composition to the bath and producing a concentrate which was more concentrated than the plating bath. (In addition, the plating bath during this test appears to be significantly

higher in zinc than the nominal level given above). The quality of distillate produced was quite good. Zinc and total solids concentrations were below their respective detection limits, but cyanide, conductivity, and hydroxide ion were detectable. The rejections or removal efficiencies were quite high; particularly for zinc and total solids. The quality of distillate was considered quite suitable for final rinsing.

Total Recycle Tests at 10% of Bath Concentration

Total recycle tests were periodically conducted in order to evaluate membrane module performance under well defined conditions of feed concentration (10% of bath concentration), pressure (700 psi), temperature (75 - 85° F), and recirculation rate through the modules (10 gpm). Results for flux as a function of time are shown in Figure 4. The flux was calculated from the measured permeate flow rate using a surface area of 70 ft² per module. (Actual surface areas measured after the field test for Modules #2 and #3 were 73 and 69 ft², respectively.) The data were corrected to 75° F using the inverse relation between flux and water viscosity.

For Modules #1 and #2 the flux levels were nearly identical throughout the field demonstration. The flux gradually declined from 13 gfd to 7 gfd over the first 3,000 hours. Following cleaning at 3,000 hours, the flux increased to 12 gfd, which is very close to the original level. Thus the cleaning procedure employed was quite successful in restoring the flux. It may therefore be
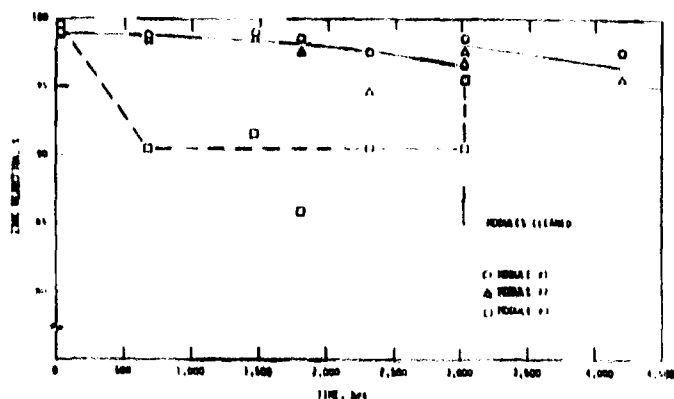
concluded that the major reason for flux decline is fouling of the membranes.

Results for Module #3 are also presented in Figure 4 (dashed line). The flux starts at a significantly higher level (20 gfd) but declines more rapidly to a value of 5 gfd at 3,000 hours. The cleaning procedure was ineffective in restoring the flux of Module #3. Because of its low flux and low rejections (discussed below) Module #3 was removed from the system at 3,000 hours.

After cleaning, the system was returned to closed-loop operation on the actual rinsewater. During the next 1,200 hours the flux for Modules #1 and #2 declined to about 7 gfd. The rate of flux decline was more rapid during this time period since a coarser grade (20μ vs 1μ) cartridge filter was used to pre-filter the feed during this segment of the demonstration.

Results for zinc rejection during the field demonstration are shown in Figure 5. For Modules #1 and #2 the zinc rejections agree reasonably well and are correlated with a single curve (solid line). The zinc rejection declined gradually from an initial value of 99% to 97% after 3,000 hours. Upon cleaning, the rejection for Module #1 increased to nearly 99% while the rejection for Module #2 increased to about 98%. Thus the cleaning procedure was successful in restoring the zinc rejection. Therefore it is reasonable to conclude that the loss of zinc rejection is primarily the result of membrane fouling. After cleaning the rejection again declined as fouling occurred.

For Module #3 the zinc rejection dropped off rapidly to a value of 90% after only 700 hours and remained reasonably constant between 700 and 3,000 hours. Cleaning produced a significant increase in rejection (from 90 to 95%).

The rejection of free cyanide is shown in Figure 6. Again the results for Modules #1 and #2 agree quite well throughout the test. For these modules the cyanide rejection declined slightly—from 98% to 97%—during the first 3,000 hours. Cleaning had little effect on the rejection level. However, because of the small loss in rejection, cleaning would be anticipated to have only a minor effect on rejection levels. Following cleaning, the cyanide rejection declined at a more rapid rate, probably as the result of the increased rate of fouling.

Fig. 4—Zinc rejection vs. exposure time as determined by total recycle tests at 10% of bath.
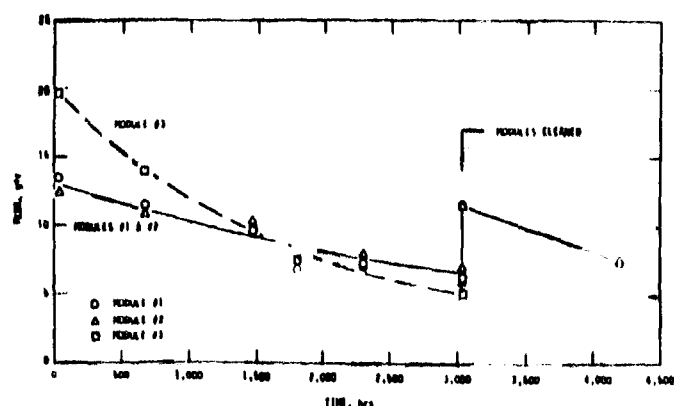
Fig. 5—Flux as a function of exposure time for total recycle tests at 10% of bath and 75° F.
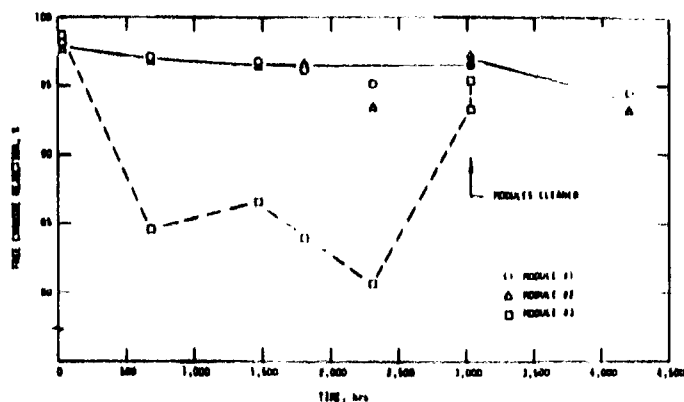
Fig. 6—Free cyanide rejection vs. exposure time as determined by total recycle tests at 10% of bath.
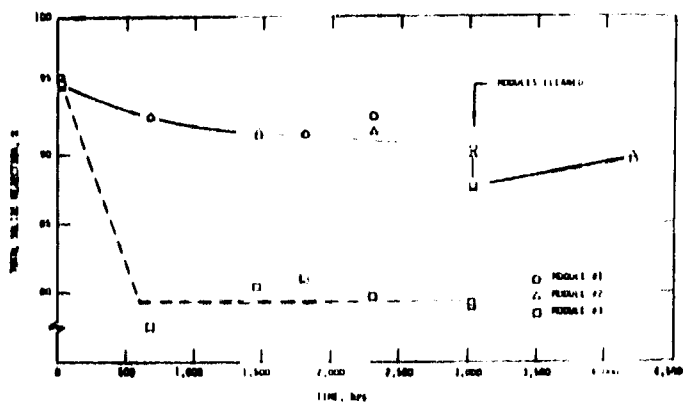
Fig. 7—Total solids rejection vs. exposure time as determined by total recycle tests at 10% of bath.

The cyanide rejection results for Module #3 are also shown in Figure 6. As for zinc, the cyanide rejection dropped quite rapidly, from 99 to 85%, during the first 700 hours and appeared to stabilize at about 85% until 3,000 hours. The data point at 3,000 hours (93% rejection) indicates a substantial recovery in rejection before cleaning. Since no similar recovery was observed for zinc and total solids rejections, it is possible that the high cyanide rejections at 3,000 hours could be attributed to a sampling or analytical error.

Total solids rejections are presented in Figure 7. The results for Modules #1 and #2 are, as before, almost identical. There was a gradual loss in total solids rejection for Modules #1 and #2 from 95% initially to 90% after 3,000 hours. Cleaning at 3,000 hours produced an apparent loss in rejection. (A similar loss was also noted for conductivity rejection.) During operation after cleaning, the rejection increased to 90%—the same level as before cleaning. Thus the loss of rejection upon cleaning was only temporary. Indeed, since the results of Figures 4-6 indicate fouling and a decline in membrane performance between 3,000 and 4,200 hours, it is reasonable to postulate that a similar decline in total solids rejection occurred during this period. By virtue of the fact that the rejection at 4,200 hours is the same as at 3,000 hours, it can be concluded that the cleaning actually improved the total solids rejection. The observed loss in rejection is probably the result of an interaction between the citric acid cleaning solution and the membrane surface. Similar results have been observed with citric acid in cleaning tests conducted by the manufacturer (7). These tests consistently showed a loss in rejection after cleaning, but the rejection then increased over a relatively short period (5-24 hours) to the level expected for a clean module. The mechanisms of this interaction is not well understood, but the rejection loss appears totally reversible by extensive flushing or by returning the system to operation on the normal feed. Thus the most reasonable explanation of the total solids rejection behavior is that, when the system was returned to normal operation after cleaning, the rejection increased to a level probably close to 95% within 24 hours and then decreased gradually to 90% at 4,200 hours as fouling of the module occurred.

The total solids rejections for Module #3 are quite similar to the zinc and cyanide rejections for this module. The rejection decreased from 95% to about 80% during the first 700 hours and remained at about 80% until the module was removed at 3,000 hours. Cleaning produced no significant change in total solids rejection for Module #3.

The close agreement between the results for Modules #1 and #2 would be anticipated for two identical modules operated in series. By comparison the results for Module #3 are quite poor. Since the system conversion per pass was low (high recirculation flow relative to permeate flow) the feed concentrations to the three modules were approximately the same; therefore a higher feed concentration would not account for the poor performance of Module #3.

A similar rapid loss in performance has been occasionally noted for some of the earlier PA-300 modules used in water disalination (7). This problem was traced to a procedure used in manufacturing the modules. The procedure has since been changed and the problem thereby eliminated. However, the modules used in this field test were manufactured before this change, and it is believed that Module #3 was defective from the outset of the test.

The level of suspended solids in the zinc cyanide bath was high compared to the levels observed for copper cyanide baths (5). A purifier (polysulfide) was regularly added to the zinc cyanide bath and produced a mud-like sludge that was removed by filtration. Some of this sludge was carried over into the rinse tanks and thus into the RO system. During the first 3,000 hours of the test, 1 μ cartridge filters were used and had to be changed approximately once per week (assuming 100 operating hours per week). After about 3,000 hours, 20 μ cartridge filter were used. The service time for the coarser filters was substantially longer (estimated service time = one month) but the rate of fouling of the modules was greater with the coarser filters. It is recommended that two cartridge filters in series—a 20 μ filter followed by a 1 μ filter—be used for pre-filtration of zinc cyanide rinsewater.

Following the field test Module #2 was cut open and

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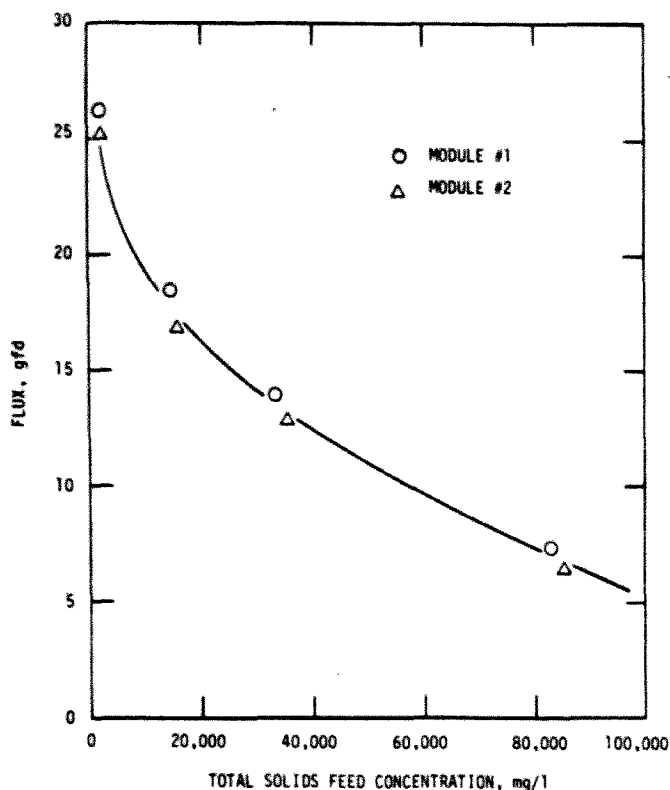
Fig. 8—Dependence of flux on feed concentration.

Fig. 9—Dependence of rejection on feed concentration.

unwound for inspection. The membrane was fouled with a thin layer of sulfide sludge with the degree of fouling increasing toward the center of the module. This layer could be very easily wiped from the membrane surface. During cleaning at 3,000 hours, a distinct odor of H_2S was noted during recycling of the citric acid solution. This is presumed to be the result of solubilization of some of the sulfide foulant. This suggests that the ammoniated citric acid was the active ingredient in the cleaning procedure and that Titron X-100 surfactant could be eliminated. Cleaning agents other than citric acid could work as well or better and should be tested. Of particular interest would be the use of oxidizing agents to oxidize the sulfide foulant layer. While the membrane is susceptible to rapid attack by some oxidizing agents such as chlorine, it has been shown to be resistant to others such as chlorine dioxide and chromic acid (6, 7).

In addition to fouling of the membrane, examination of the module internals revealed some possible deterioration of the membrane backing material. Samples of the membrane and backing were returned to the manufacturer for examination, the finding of which confirmed that the backing had been deteriorated, probably as a result of the high concentrations of hydroxide ion in the rinsewaters (7). However, it is not clear what effect deterioration of the backing would have on membrane module performance. No gross effects on performance were observed during the field test. Substitute backing materials could be used, but a development program would be required to commercialize the PA-300 on a more resistant backing.

Total Recycle Tests at Other Feed Concentrations

Following initial start up of the RO system, total recycle tests were conducted to determine the dependence of flux and rejection on feed concentration. Tests were conducted at various dilutions of the plating bath ranging in nominal concentration from zero to 20% of the bath concentration.

Flux results as a function of the total solids concentration of the feed are shown for Modules #1 and # 2 in Figure 8. The results for these two modules are in very good agreement. (Results for Module #3 were not consistent with those shown in Figure 8 and have not been included). As expected, the flux decreases with increasing feed concentration and approaches a level generally considered uneconomical at a feed concentration in the vicinity of 100,000 mg/l. By comparison the bath concentration is approximately 350,000 mg/l in total solids. These data illustrate the problem of using RO to achieve very high concentrations. The data presented in Figure 8 can be used in optimizing the degree of concentration that should be obtained in the RO system prior to evaporation.

Rejection as a function of the total solids concentration in the feed is shown in Figure 9 for Modules #1 and #2. The zinc, cyanide, and total solid rejections remain essentially constant at 99%, 98%, and 95%, respectively for feed concentrations below about 40,000 mg/l total solids. At higher feed concentrations the rejections drop off as expected.

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Economics

One of the main objectives of conducting a field demonstration is to provide a basis for evaluating the economics of the process. Figure 10a shows the flow schematic for the original two-stage countercurrent rinsing system. The rinsewater flow rate was measured at 2.0 gpm. The rate of dragout from the bath was estimated by turning off the rinsewater and measuring the buildup of zinc and total solids in the first rinse as a function of time. The calculated dragout rate was 0.01 to 0.015 gpm. However the parts being plated during this determination were flat and free-draining and a somewhat higher dragout rate of 0.02 gpm was considered more typical for purposes of design. Given these flow rates and ideal mixing in the rinse tanks, the zinc concentration is reduced from 20,000 mg/l in the bath to 2.0 mg/l in the final rinse.

Figure 10b shows the flow schematic, flow rates (in gpm), and zinc concentrations (in mg/l) for an RO/Evaporator system designed to give the same zinc concentration in the final rinse. The flow rates given in Figure 10b are for 90% water recovery in the RO system (ratio of system permeate to system feed: 5.85/6.5 = 0.90). All of the concentrate from the RO system is converted to distillate in the evaporator, and an equal flow (0.65 gpm) of plating bath is used to purge the concentrated chemicals from the evaporator and prevent precipitation. The stream returning to the bath is about 3% higher in concentration than the bath, and precipitation in the evaporator would occur only if there were some constituent in the bath (e.g., carbonates) at a concentration very close to its solubility limit. The permeate and distillate flow rates given in Figure 10b (5.85 and 0.65 gpm, respectively) are considerably greater than the corresponding flows in the system demonstrated (1-1.5 and 0.2 gpm, respectively).

One of the most important of design criteria is the flux for the RO system. The flux depends on the operating pressure, temperature, feed concentration, and the flow rate of concentrate from the module. The system would be designed to operate at 800 psi, maximum recommended operating pressure for the modules. The design temperature would be 77° F. At higher temperatures the flux would increase, and the rejection would remain essentially the same. Thus the performance of the RO system would improve with increasing temperature, although the membrane life may be shortened. For the design case shown in Figure 10b (i.e. 90% RO system conversion) the total solids concentration in the feed to the first RO module is calculated to be 5,500 mg/l and the concentrate withdrawn from the final module is 10,600 mg/l. Thus the average feed-side total solids concentration is about 8,000 mg/l. From Figure 8 the flux for a new module at this feed concentration would be about 20 gfd (at 700 psi and a recirculation flow rate of 10 gpm). From Figure 4 the flux declines to about half of its initial value over an operating period of about 700 hours (exposure time: 3,000 hours). Thus it would seem reasonable to design the

a. Present rinsing system

b. Closed-loop rinsing system
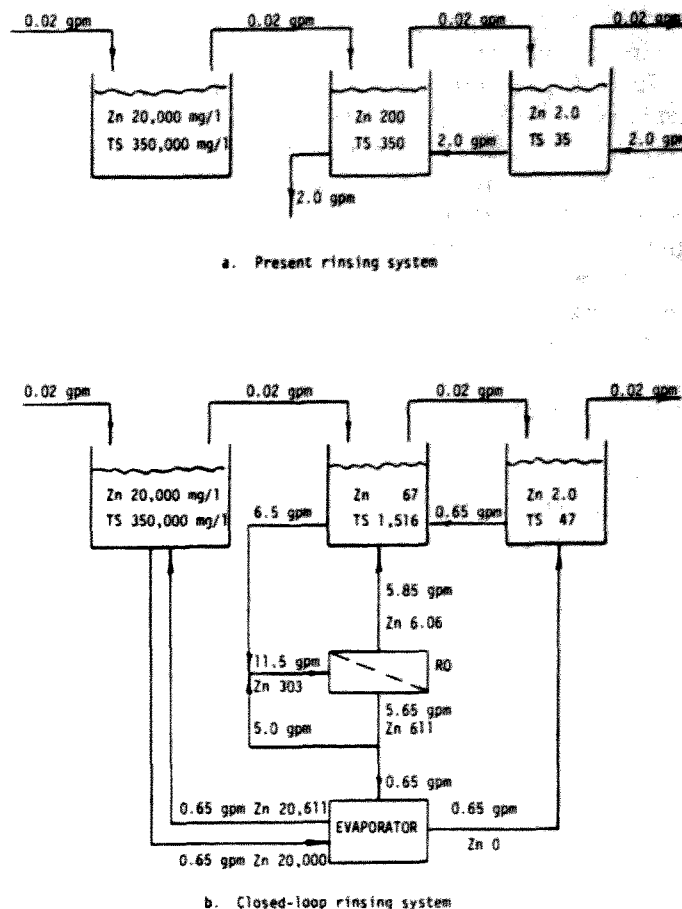
Fig. 10—Flows and concentrations for open and closed-loop rinsing.

system for a minimum flux of 10 gfd. At this flux the rate of permeate production is approximately 0.5 gpm for each module (area = 70 ft²). Based on the recommended ratio of concentrate flow to permeate flow (10 to 1) the rate of recirculation for the RO system would be 5 gpm as shown in Figure 10b. (This recirculation rate is only half of that used during this field demonstration and could result in a slightly lower flux than measured; however the higher operating pressure—800 vs 700 psi—would compensate by increasing the flux.)

Rejection is also an important parameter in the design. Based on the results of Figure 9 at a total solids concentration of 8,000 mg/l, the zinc and total solids rejections would be 99% and 95%, respectively. From Figures 5 and 7, fouling of the modules can be expected to result in a decrease in zinc rejection from 99 to 98%. Thus, for the design, the minimum zinc and total solids rejections were selected as 98% and 90%, respectively.

The RO system can be designed to operate at any desired conversion within reason. At low conversion the capital and operating costs are dominated by the evaporator; at high conversion, capital and operating costs are dominated by the RO system. At some intermediate conversion, the total operating cost should pass through a minimum. Material balance calculations were performed for the system of Figure 10b using various RO system conversions. (Results are shown only for the 90% conversion case.) Capital and operating costs

were then developed for each conversion in order to determine the optimum.

Table 2 gives the capital costs for the RO unit, the evaporator unit, and the total system, for various RO system conversions. The material balance relationships and the RO module rejection were used to calculate the permeate flow and the evaporator capacity required to give a zinc concentration of 2 mg/1 in the final rinse. At zero conversion in the RO system (i.e. no RO system) the entire treatment load is handled by the evaporator. For this case the evaporator must produce 2.0 gpm in order to provide the same degree of rinsing as the original 2-stage countercurrent system. Cost details are noted at the foot of Table 2. The lowest capital cost occurs when the evaporator is used to handle the entire treatment load. For RO system conversion between 70 and 90%, the total system cost remains at about $62,000.

Total annual operating costs were also calculated for each RO system conversion. The breakdown of operating costs for a conversion of 90% is shown in Table 3. Specific costs and assumptions are noted at the foot of Table 3. The costs are based on operating 100 hours per week (Monday morning through Friday afternoon) and 50 weeks per year for a total of 5,000 operating hours per year. Similar operating costs were developed for other RO system conversions.

The electrical costs for the RO system are strongly dominated by the requirements for the high pressure pump. The use of a positive displacement pump was assumed with a combined pump/motor efficiency of 75%. In addition, since a new (or clean) module would produce twice the design flux, the RO system could be operated at half the design pressure (i.e., 400 psi). As fouling occurs the operating pressure would be increased to maintain the design flux, and the system would be cleaned when the operating pressure reached 800 psi. Thus an average feed pressure of 600 psi was used in calculating the power costs of Table 3.

When operating with the 1μ cartridge pre-filters, it was necessary to change the two parallel cartridges after about 100 hours of operation. With the 20μ filters, the pressure drop was still quite low (< 3 psi) even after 300 hours of operation. With two parallel passes each having a 20μ and a 1μ cartridge in series, it is estimated that the four filters would last for about a month (400 hours). Monthly replacement was therefore assumed for the economic calculations.

With 1μ pre-filtration, cleaning was required after about 700 hours of operation. During this time three modules were in use. However for the design cases shown in Table 2, anywhere from 6 to 18 modules would be used. It is reasonable to postulate that the extent of fouling would vary inversely with the membrane surface area. Thus a cleaning frequency of once every four months (1600 hours) was assumed.

Membrane life is a very important parameter in the economics. As mentioned above, chemical attack of the membrane or other module components would be expected to depend on total time of exposure to the rinsewaters rather than operating time per se. The two field demonstration modules were exposed to the rinsewaters for a total of 4,200 hours. This is close to the 5,000 hours operating time per year taken as the basis for calculating the operating costs. If the system were designed to purge the modules with distillate on shutdown, the effective exposure time would also be about 5,000 hours. Thus a membrane life of one year would be virtually assured. However, it is likely that the membrane life would be considerably longer than one year. During the field demonstration the modules produced only a fraction of the permeate flow that would be produced by a system designed to meet the rinsing constraints of Figure 10b. Thus the feed concentration to the field demonstration modules was considerably greater than would be seen by a larger capacity system. Furthermore, during periods when the demonstration system was not

TABLE 2
CAPITAL COSTS FOR VARIOUS RO SYSTEM CONVERSIONS

RO System Conversion	Required Permeate Flow gpm	Required [a] Membrane Area ft²	Required [b] No. of Modules	Membrane [c] Module Cost $	Housing [d] Cost $	Total Cost [e] for RO System $	Required [f] Evaporator Capacity gph	Total Cost for Evaporator $	Total System Cost $
0							120	44,129	44,129
0.70	2.575	371	6	3,780	1,700	21,780	66.2	39,199	69,979
0.80	3.625	522	8	5,040	2,550	23,890	54.4	39,199	63,089
0.90	5.85	842	12	7,560	3,400	28,560	39.0	33,880	62,440
0.95	8.91	1,283	18	11,340	5,100	34,040	28.1	33,880	67,920

(a) Design flux = 10 gfd.
(b) Based on area of 70 ft² per module.
(c) Based on $630 per module (Abcor, Inc.)
(d) Based on $850 per 3-module housing (The Permutit Co., Inc.).
(e) Based on system cost of $15,000 (Osmonics, Inc.) for system W/O modules, housings, and high-pressure pump. Pump/motor cost = $1,300 for < 4 gpm permeate; $2,600 for > 4 gpm permeate (Wanner Engineering, Inc.).
(f) Double effect evaporator with cooling tower package. Based on rated capacities of 200 gph ($44,129), 100 gph ($39,199), and 50 gph ($33,880).

operating, the concentration across the membranes equilibriated resulting in very high concentrations on the permeate side. This situation would accelerate attack of the membrane backing material and other permeate-side components. Purging the system on shut-down would largely eliminate this source of module deterioration.

Considering these factors, it is not unreasonable to project a two-year membrane life as assumed in Table 3.

Operating and maintenance labor for the RO system was assumed to require 1 day per month. This would include system start-up on Mondays, shut-down on Fridays, cartridge filter replacement, membrane cleaning, and other maintenance as required.

Steam consumption for a double effect evaporator operating as shown in Figure 10b with temperatures of 130° F and 110° F in the first and second effects, respectively was calculated to be 0.66 lbs steam/lb distillate. Electrical requirements for operation of the cooling tower, evaluation of the evaporator, pumping the various output streams, and miscellaneous usage were obtained from the manufacturer (4.64 kw, 8.64 kw, and 16.64 kw for double effect capacities of 50, 100, and 200 gph, respectively). As for RO, operation and

TABLE 3
TOTAL AND NET OPERATING COST FOR 90% RO SYSTEM CONVERSION (5,000 OPERATING HOURS PER YEAR)

Item	RO System $	Evaporator System $	Total System $
Capital Amortization (a)	2,100	3,388	5,488
Direct Operating Costs			
Steam @ $3.50/1000 lbs (b)	-	3,760	3,760
Electrical @ $0.0474/kw-hr (c)	1,008	1,100	2,108
Operation & Maintenance @ $10/hr including fringe benefits (d)	960	960	1,920
Cartridge Filters & Cleaning Chemicals (e)	240		240
Membrane Replacement (2-year life)	3,780		3,780
Total Direct Operating Cost	5,998	5,820	11,808
Total Annual Operating Cost	8,098	9,208	17,296
Credit for Bath Recovery @ $0.47/gal (f)			(2,820)
Credit for Water Recovery @ $0.45/100 ft³			(361)
Credit for Cyanide Destruction @ $4.05/lb CN (g)			(6,440)
Credit for Solid Waste Disposal @ $29/drum and 25% solids in sludge (h)			(354)
Total Annual Credits			(9,975)
Net Annual Operating Cost			7,321

(a) Straight-line depreciation over 10 years with zero salvage value.
(b) Based on actual cost for No. 4 fuel oil of $0.393/gal, heating value of 140,000 Btu/gal, and a boiler efficiency of 80%.
(c) Based on actual cost for October 1978.
(d) Based on actual maintenance labor rates.
(e) Four cartridge filters changed once per month at average cost of $4.68 each. Cleaning three times per year with 6 lbs citric acid per cleaning at $0.82 per pound.
(f) Chemical costs: zinc $0.445/lb; sodium cyanide $0.51/lb; caustic $0.185/lb; brightener $6.792/gal.
(g) Based on 8 lbs NaOCl per lb of CN with no addition of caustic (already present in rinsewater). Cost for 15% NaOCl solution = $0.665/gal.
(h) Based on sludge centrifuged to 25% solids and hauled in lots of 80 55-gal drums.

Fig. 11—Annual operating costs for various RO conversions.

maintenance for the evaporator was assumed to require one man-day per month.

As shown in Table 3, the direct operating costs (excluding amortization) are about $6,000 per year each for the RO system and the evaporator for a total of about $12,000. The total annual operating cost including amortization is $17,300. Table 3 also gives the breakdown of credits resulting from recovery of the rinsewater. The largest credit results from a reduction in the amount of cyanide to be destroyed. The credit for sludge disposal was calculated on the basis of the weight of zinc hydroxide produced by precipitation of the dragout and is probably significantly less than for plating shops which do not have solids dewatering equipment. The total annual credit for rinsewater recovery is about $10,000, which leaves a net operating expense of $7,300 per year for the recovery system.

Operating costs were also determined for other RO system conversions and are shown in Figure 11. For conversions ranging from 70% to 95% the RO operating costs increase and the evaporator operating costs decrease. The total operating cost passes through a minimum at an RO system conversion of 90%. Using an evaporator alone for rinsewater recovery (zero percent RO system conversion) the total annual operating cost including amortization is about $20,900. For the optimum combination of RO and evaporation, the total annual operating cost is approximately $17,300 which represents in annual savings of $3,600.

In considering the impact of these numbers it should be emphasized that the recovery system was designed to meet a given rinsing criteria for a two-stage countercurrent rinsing system. Recovery system costs could be reduced significantly by using more rinsing stages. For manual operations, additional rinse tanks could be inserted in the line, and for automatic operations, over-the-tank spray rinses could be used. In addition, consideration should be given to working with higher rinse concentrations where rinsing is not critical. The costs for recovery provide a substantial incentive for reducing the rinsewater flow by simple, inexpensive techniques.

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Membrane Processes for Metal Recovery
From Electroplating Rinse Water

John L. Eisenmann*

Investigations into the feasibility of two new applications of membrane processes for the recovery of plating metals from electroplating rinses have recently been initiated with the aid of EPA demonstration grants. These are the recovery of chromic acid from a decorative chrome plating line by electrodialysis and the removal of nickel from a Watts-type line via Donnan Dialysis. Both of these processes function by transferring metal ions or metal containing ionic complexes across ion-exchange membranes. This ionic transport is from the rinse water on one side of the membrane to a receiving solution on the opposite side. The enriched solution can then be returned to the plating tanks or otherwise treated more conveniently or economically than the rinse stream itself. A major difference between the two processes is that the driving force for electrodialysis is an impressed electrical potential across the membrane while Donnan dialysis depends on maintaining a cross-membrane concentration gradient. As normally operated, electrodialysis functions as a demineralization process, removing and concentrating both anions and cations from the treated solution. Donnan dialysis acts as a continuous ion-exchange process, replacing the ionic constituent of interest with an innocuous or a less valuable species of the same charge type. Lately, electrodialysis appears to have become more familiar to the electroplating industry but Donnan dialysis has seen little, if any, exploitation in this area. One of the goals of the demonstration programs is to make potential users aware of the technology and to indicate where it might best be applied. Each process will be discussed in more detail below and some of the laboratory and field results to date described.

Electrodialysis (ED) is a membrane process which can be used for the separation, removal or concentration of ionized species in water solutions. These operations are accomplished by the selective transport of the ions through ion-exchange membranes under the influence of an electrical potential (VDC) applied across the membrane. The ion-exchange membranes are the key to the process and two types are required. Cation-exchange membranes, which are permeable only to the positively

charged cations in the solution, and anion-exchange membranes which permit only the passage of negative, anionic species. Physically, both membrane types are formed as thin sheets of ion-exchange material, usually reinforced by a synthetic fabric backing to provide the necessary strength. Thickness can vary between one-tenth to almost on millimeter and membrane sheets larger than one meter square are commonly used. The resin matrix is usually styrene or vinyl-pyridine copolymerized and cross-linked with divinylbenzene and the exchange capacity imparted by sulfonic acid, or quaternary ammonium or pyridinium groups covalently bonded to the polymeric backbone. In such membranes, 95-99% of any electric current flowing is carried by the mobile counterions.

In the usual configuration for electrodialysis, alternating cation- and anion-selective membranes are arrayed in parallel between two electrodes to form an ED multicell or membrane "stack" (1,2). Especially designed spacer/gaskets separate the membranes by forming leak-tight, flow directing compartments between adjacent membranes, and the whole assembly is held in compression by a pair of end plates and tie-rods or other clamping device. The compartments or cells formed by the spacers are typically 1-1.5 mm thick and direct the solution fed to the cell over the surfaces of the membranes either in a tortuous path or sheet flow pattern. The flow path usually contains a plastic screen or supporting baffles to ensure separation of the membranes and induce turbulent flow. A stainless steel sheet is commonly used for the cathode and platinized titanium for the anode. Other necessary equipment such as pumps, power supply, filters and piping is conventional, but plastic components are used wherever possible to avoid corrosion, stray electrical currents and contamination of the process streams.

Conventional arrangement and operation of an ED multicell are shown schematically in Figure 1. The process or feed solution which is to be depleted of ions is fed to the even-numbered or diluting cells and the ion-receiving or concentrating solution passes through the odd-numbered cells. Usually the same solution is used for both streams but the concentrating solution is volumetrically 10% to 20% of the feed and may be recycled to minimize the amount of discharge and better control the pressure differential. The repeating stack unit of a cation-selective membrane, a diluting spacer, an

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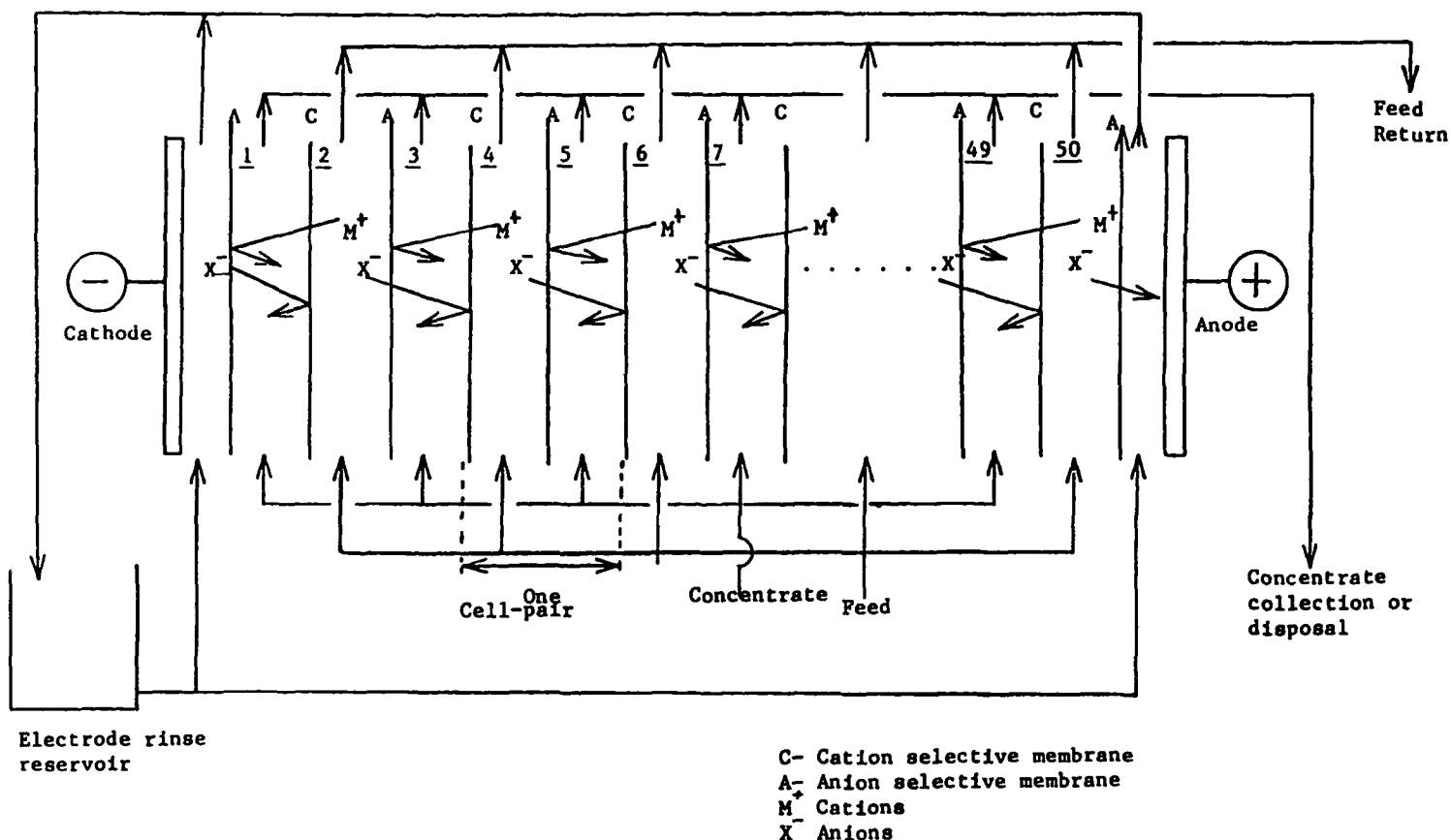176 King Street, Hanover, MA 02339

Fig. 1—ED Multicell Schematic.

C- Cation selective membrane
A- Anion selective membrane
M⁺ Cations
X⁻ Anions

Electrode rinse
reservoir

anion-selective membrane, and a concentrating spacer is termed a cell-pair, and ED equipment can be characterized by indicating the number of cell-pairs comprising a multicell. Industrial stacks generally contain 50-300 cell-pairs although a recent report has described a multicell containing over 900 cell-pairs especially designed for large-volume brackish water demineralization. Solution is distributed to, and collected from, the cells by two internal hydraulic circuits; one for the concentrating cells and one for the diluting cells. As indicated in Figure 1, the passage of a direct current through the stack causes the ions in the solutions flowing through the stack to move in the direction of the oppositely charged electrode. Positive cations in the feed stream are attracted to the negative cathode and pass from the diluting compartments, through the cation-exchange membranes on the cathode side of the cell, into the concentrating compartments, where they accumulate, since their further transport is prevented by interposed anion-selective membranes. Negative anions move in the opposite direction, traversing the adjacent anion-exchange membranes but blocked by the cation-exchange membrane next encountered. Flow velocity of the solutions in the cells varies with the stack type within the range 5-50 cm/sec. A hydraulically separate stream is used to rinse the electrode compartments and remove the gases formed by the electrode reactions:

at the cathode: $2\ H_2O + 2e^- \rightarrow H_2\uparrow + 2OH$

at the anode: $H_2O - 2e^- \rightarrow 1/2\ O_2\uparrow + 2\ H^+$ or
$Cl^- - e^- \rightarrow 1/2\ Cl_2\uparrow$

The electrode rinse is usually acidified to prevent increases in pH and resulting precipitation of insoluble species. Part of the feed or concentrate solutions can be used as the rinse or a special rinse solution prepared and recycled independent of the process streams. Use of the electrodialysis multicell concept makes it possible to obtain a deionizing effect equal to many times the electrical equivalents passed. This feature and the availability of physically strong and highly selective ion-exchange membranes combine to make electrodialysis economically viable, notably for the desalination of water.

Ohm's and Faraday's Laws apply to the electrochemical phenomena occuring within the multicell and several mathematical relationships can be used to characterize electrodialysis equipment and to compare different types of apparatus. Current efficiency, also called coulomb efficiency, indicates the effective utilization of the current passing through the membrane stack for transfer of the ion of interest. It is calculated from feed stream flow rate and inlet and outlet concentrations, current through the stack, and number of cell pairs.

Another important consideration is the relationship of the stack limiting current density to solution concentration and flow velocity. If the limiting current

density is exceeded, polarization at the membrane surface will occur due to local ion depletion and pH changes, precipitation in the cells, high electrical resistance and loss of current efficiency may result. To avoid polarization operating current densities are held at conservative levels, often one-half the limiting value. Turbulance promoters and high fluid velocities in the feed cells are used in an effort to maximize the allowable current through the stack.

For the treatment of plating rinse water, rather small, mobile ED modules have been developed for use in the usually space-limited plating rooms. A commercial unit is shown in Figure 2. It measures approximately 42" × 52" × 27" and contains all controls and equipment necessary for operation. Feed and return piping for recirculation of a still or reclaim rinse and a single electrical connection are all that are necessary to complete installation. The membrane stack shown at the lower right of the module contains 35 cell-pairs and can vary in size in order to provide the capacity required to remove an amount of plating salts equal to that dragged into the rinse from the plate tank(s) and thus hold the reclaim solution at a constant metal concentration. The multi-cell differs from conventional ED equipment in that the concentrate cells are dead-ended for maximum concentration and simplified operation.

In order to extend the electrodialysis concept to the treatment of chrome plating rinses, one of the first considerations was the chemical resistance of the membranes. To check this, commercially available anion-exchange membranes were immersed at room temperature in chromic acid plate solution and sections removed for testing after 7, 14, 42, and 69 days. All sections were leak-tight and appeared to have lost none of their physical strength although there was a slight roughening of the surface. Exchange reactions indicated that the ion-exchange groups were not affected by the acid. Laboratory electrodialysis experiments were then conducted with a five cell-pair stack similar in size and operating characteristics to the multicell shown in Figure 2. Simulated chromic acid rinse solutions were prepared by dissolving chromium trioxide in tap water. Electrodialysis of these solutions over a range of current densities gave the representative results in Table I. All samples were taken after several hours operation at each operating condition. Rinse temperature was 78-91° F. The data indicate that chromic acid can be concentrated from dilute aqueous solutions at least to about 70% of the strength of many chrome plate solutions and may be useful for direct return to the plate tanks. Figure 3 plots the increase in product concentration with current through the stack, a result consistent with data from other electrodialysis concentration experiments. (3) The attainable chromic acid concentration in the product appears to be leveling off at 170-180 g/l and the product/feed concentration ratio decreases with increasing feed concentration. During the course of these experiments the membranes were in contact with varying concentrations of chromic acid over a period of 2-3 months without obvious deterioration or loss of selectivity; tending to confirm the life test results described above.

A fifty cell-pair demonstration module was next constructed for testing on an actual chrome plating line operated by Seaboard Metal Finishing Co. of West Haven, CT. This module is shown on-site in Figure 4 and was installed to recirculate a dead rinse located between the plate tanks and the counterflow rinses. Figure 5 is a schematic of this arrangement. Recirculation rate through the ED stack was 20-25 GPM and dilute sulfuric acid was used an an electrode rinse solution. Initially, the objective was to determine if the membranes and other materials of construction would be sufficiently resistant
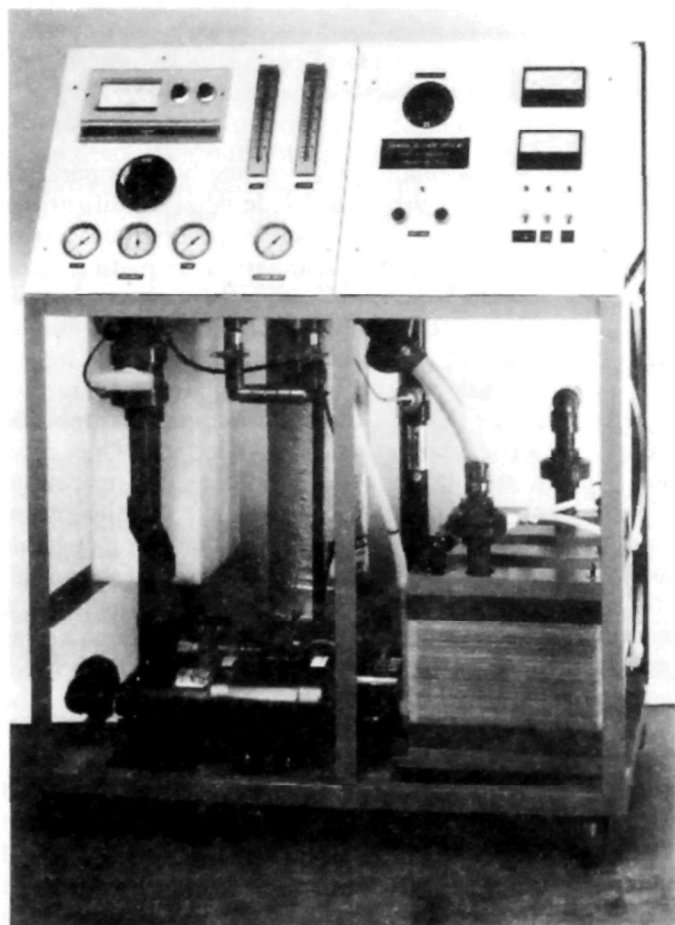
Fig. 2—Electrodialysis Module for Metal Recovery.

Table I
Electrodialysis of Simulated Chromic Acid Rinses

Run	Current Density	Feed Conc. g/l CrO₃	Product Conc. g/l CrO₃	Product/ Rinse Ratio
1	10 ma/cm²	.37	61	165
2	12	.32	106	331
3	14	1.24	143	115
4	16	.98	167	170
5	18	.70	174	249
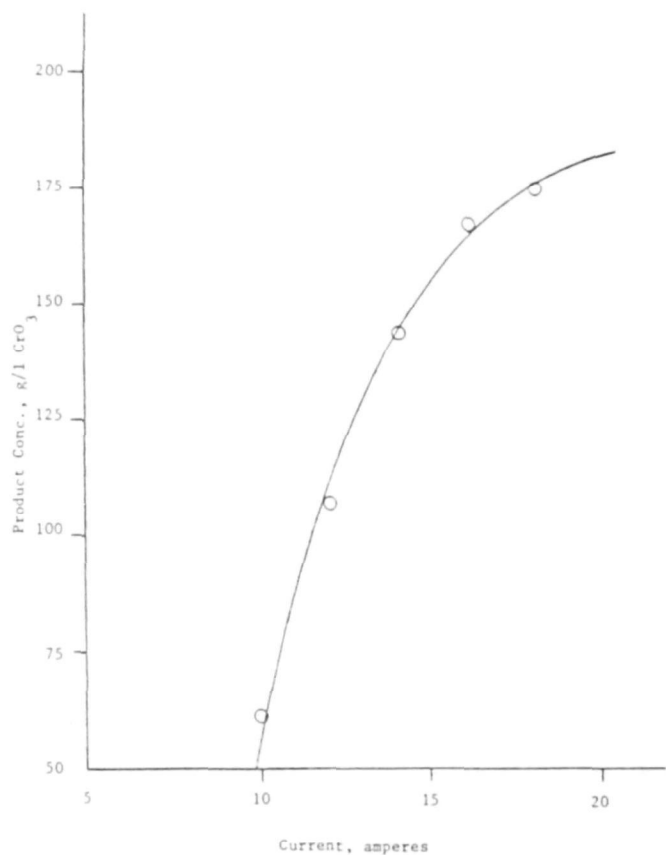
Fig. 3—Chromic Acid Electrodialysis
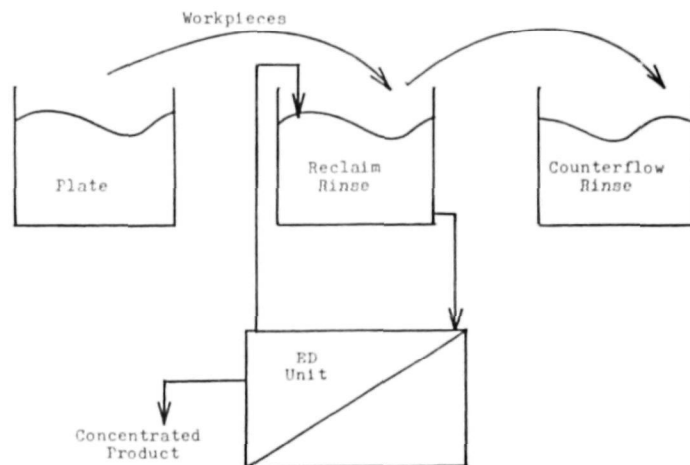
Fig. 5—ED Treatment of Chrome Line.
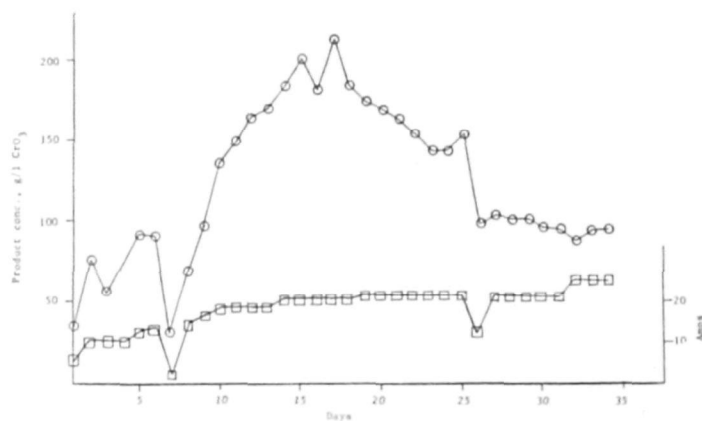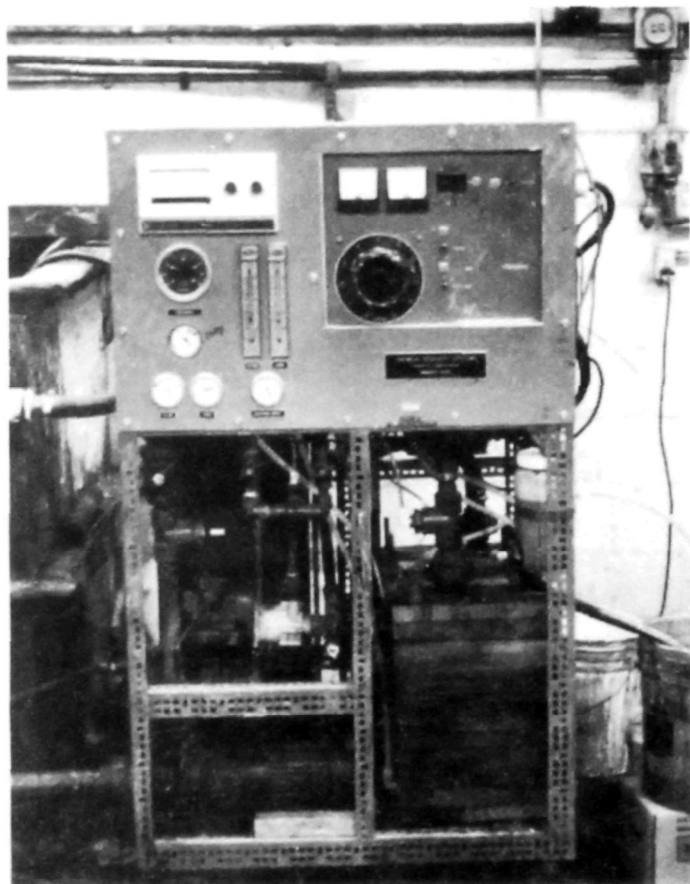

Fig. 6—Chrome Product Concentration.

Fig. 4—Electrodialysis Unit on Chrome Line.

to exhibit a reasonable life, to see what operating conditions must be used, to decide what modifications must be made to optimize chrome recovery during later stages of the project and to familiarize the plating room personnel with operation of the electrodialysis equipment. The recovery unit was to run directly on the drag-out solution without any adjustment in or accommodations by the normal plating operation. During this time the unit was run for approximately 250 hours over a period of more than two months. Operation was during the day shift of a three-shift operation. Concentrations of product samples taken at the end of each operating run together with the operating currents are plotted in Figure 6. During the first part of the period the current on the stack was increased slowly to a maximum of 20-21 amps at Day 10, where it was maintained for the remainder of the period. Product concentration also increased, as expected from the laboratory data, and remained relatively high in the 160-212 g/l chromic acid range until Day 26 when it fell sharply. The chief operating difficulty during the period was the high temperature acquired by the rinse solution due to heating by the pumps and the DC current applied to the stack. Most of the time it was significantly greater than 100° F, the recommended maximum operating temperature, and caused extensive slippage between the

stack spacers and membranes, eventually leading to external and internal leakage. It is to this leakage that the sharp drop in product concentration is attributed and, indeed, the highest observed rinse temperature of 118° was reached on the previous day. Rinse concentration data during this operating period are incomplete but were in the 50-70 g/l CrO₃ range, giving product/feed concentration ratios of 2-4. These ratios can, of course, be markedly improved by operating simultaneously with the plating operation to prevent chrome buildup in the rinse and/or increasing the stack capacity as required.

At this point the test program was interrupted for equipment inspection and evaluation, construction and installation of a new stack designed to minimize slippage problems, and installation of a cooler in the rinse tank. Disassembly of the stack revealed no general failure of the membranes but several were torn and wrinkled due to displaced spacers. Others had developed pin-holes. Some spacers had extruded to partially block the flow path and manifolds and there was a general misalignment of the stack plies, again, probably attributable to the high temperatures. At this time, or at subsequent re-startup attempts, all wetted stainless-steel flowmeter fittings had to be replaced, viton "O" installed in all unions and filters and a replacement plastic impeller housing for the feed pump was required. The second test period was started a few weeks ago but no correlated data is yet available. Plans are for the ED unit to run concurrently with the plating shifts and to increase recovery capacity by increasing membrane area with a larger stack or additional units. Lower rinse concentrations should then be able to be maintained. With the addition of the cooler in the rinse solution, higher current densities can also be explored. The outlook for use of ED for chromic acid recovery is promising but it appears that high current densities will be required to obtain a product of plating concentration, that cooling will be necessary and that, relative to treatment of other bath types, more membrane area will be needed for equivalent metal recovery.

The second membrane system being examined for potential usefulness to the electroplating industry is Donnan dialysis. This process uses the permselective properties of ion-exchange membranes to establish a Donnan equilibrium between two solutions of electrolytes separated by the membrane. In contrast to electrodialysis, only one type of membrane is used; either cation- or anion-permeable. For example, in the case of a cation-exchange membrane, the anions in the two solutions are prevented from inter-diffusing across the membrane but the mobile cations will redistribute themselves between the two solutions on either side of the membrane until equilibrium is reached and the ratios of all similarly charged cations are equal:

$$(C_{il}/C_{ir})^{1/z_i} = (C_{jl}/C_{jr})^{1/z_j} = (C_{kl}/C_{kr})^{1/z_k} = K$$

where i, j, and k are cationic species, z their valence, C their concentration and r and l refer to the left sides of the membrane.

Any multivalent ions present in the solutions will equilibrate at higher ratios than the monovalent ions. The driving force for the cation exchange is the system's displacement from the equilibrium ratios and can be controlled by manipulation of the solution concentrations. If the concentration of one cation species is substantially increased in, say, the left or stripping solution, the total cation concentration is maintained due to the impermeability of the membrane for anions and the principle of electroneutrality as applied to the solutes. However, in order to approach equilibrium, the net effect is the diffusion of any other cationic species in the right-hand solution from right to left across the membrane, against the concentration gradient, to ultimately reach a concentration many times that remaining in their original solution. They are replaced by counter-diffusion of the added cation. The major variables affecting the transfer rate are temperature, concentration and solution flow characteristics at the membrane face. In practice, membrane configuration can be plate-and-frame (similar to the ED multicell), tubular or hollow fiber and the process regarded as a continuous ion-exchange system.

The feasibility of the process has been examined in the laboratory for the separation and concentration of uranyl and lanthanum ions (4), water softening (5), nutrient removal from secondary sewage effluents (6) and, in the present case, nickel removal from plating rinses. The early tests of nickel solutions were performed on plate-and-frame apparatus adapted from the ED membrane stack shown on the module in Figure 2 and schematically in Figure 1. Commercial cation-exchange membranes in sheet form were used. Dilute nickel feed solution was pumped repeatedly through a single feed cell and 0.5-1 N H₂SO₄ stripping solution recirculated through two flanking concentrating cells. Typical results are shown in Table II.

As can be seen, a 20% reduction (% cut) in nickel per pass through the unit was realized in the feed solution by exchange with strip solution hydrogen ions and the recovered nickel was concentrated in the strip solution up to 50 times its original feed concentration. In another experiment a sulfuric acid stripping solution was recirculated for 40 hours against a once-through feed solution held between 25 and 50 mg/l nickel. The strip was maintained at 1.0 - 1.5 normal by the periodic addition of acid but no other adjustments were made. At the end of the experiment the nickel concentration in the

TABLE II NICKEL RECOVERY BY DONNAN DIALYSIS				
Ni Feed Conc., mg/l in	out	% Cut	Ni Strip Conc. mg/l	Strip/Feed (in) Conc. Ratio
30	24	20	710	24
24	19	21	780	33
20	16	20	830	42
13	10	23	870	67

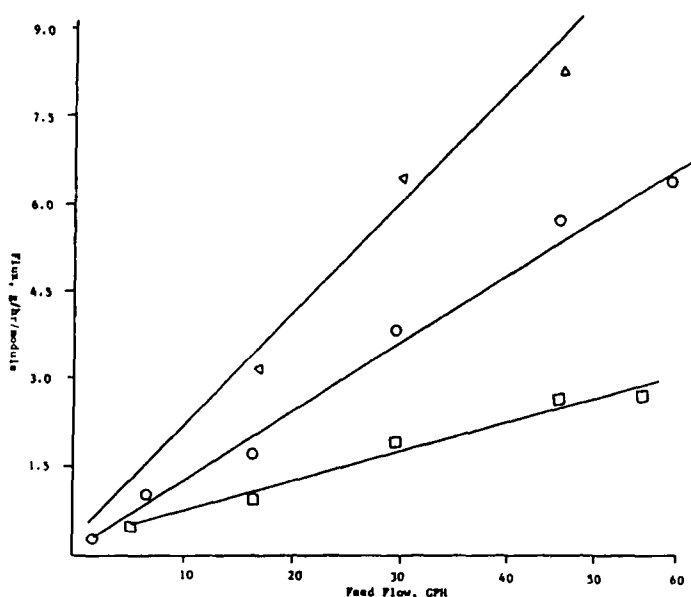Fig. 7—Nickel Recovery by Donnan Dialysis.

Fig. 8—Donnan Dialysis Transport Rate vs. Flow Rate.

flux in g/hr/380-tube module is plotted versus total feed flow rate. Each curve represents a fixed nickel concentration and at each concentration level the flux increases with flow rate. This is typical of film-controlled membrane processes where the thickness of the stagnant layer at the membrane surface can be reduced by increasing fluid velocity. The increase in flux with bulk solution concentration at equivalent flow is also consistent with a film controlled process where diffusion to the membrane face is critical.

On the basis of the laboratory results a Donnan dialysis unit was constructed for field testing to demonstrate nickel recovery from the rinse water on a Watts-type nickel plating line. The unit consists of four vertically mounted shell and tube Nafion exchangers fabricated by DuPont and piped to be able to run in parallel or in series, plus two auxiliary tubes arranged for series flow only. Each tube provides 20 ft² of membrane area. A schematic of the feed side hydraulics only is shown in Figure 9. Strip solution is always up,

strip had increased to 14 g/l, a concentration ratio of 300, without any decrease in transfer rate or percent removal, indicating no significant decrease in driving force. Feed pH was 1.75 to 6.0 during the experiment.

If, in addition to the strip, the rinse or feed solution is also recirculated, extremely low residual nickel concentrations can be attained with Donnan dialysis. Figure 7 is a plot of the nickel concentration in a simulated rinse where an initial concentration of 4 mg/l nickel was reduced to .07 mg/l after 29 hours continuous dialysis. Again, only a single cell was used and much more rapid removal rates would be anticipated with an increase in membrane area. Higher initial concentrations could also be easily treated at the expense of additional treatment time or equipment size. It is, of course, possible and perhaps sometimes desirable to flow both feed and strip solutions through the exchanger on a once-through basis. The data demonstrate the possibility of polishing some plating effluents to fractional ppm with a very simple technique and offers the hope of meeting very low effluent standards.

We have also performed some Donnan dialysis work using ion-exchange membranes in tubular form. The tubes were made by DuPont from their Nafion ion-exchange resin and had an inside diameter of .025". A shell and tube exchanger containing about 380 individual tubes, or 13 ft² of membrane area, was used. The aim was to verify the effects of certain operating variables on nickel transport rate. Results are shown in Figure 8 where

Fig. 9—Feed Side Flow Schematic.

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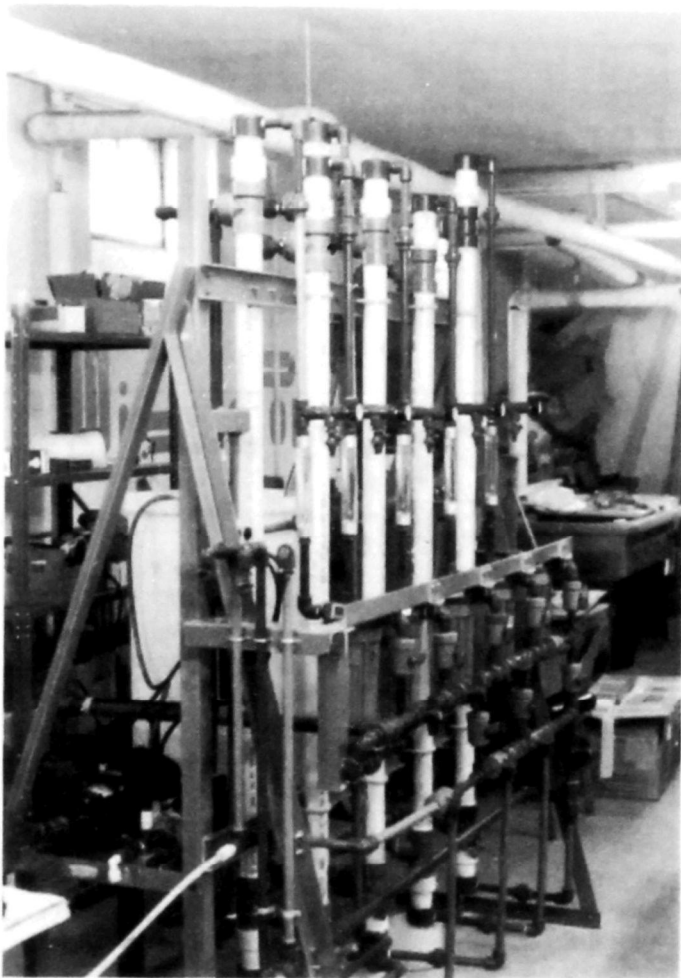
Fig. 10—Tubular Donnan Dialysis System.
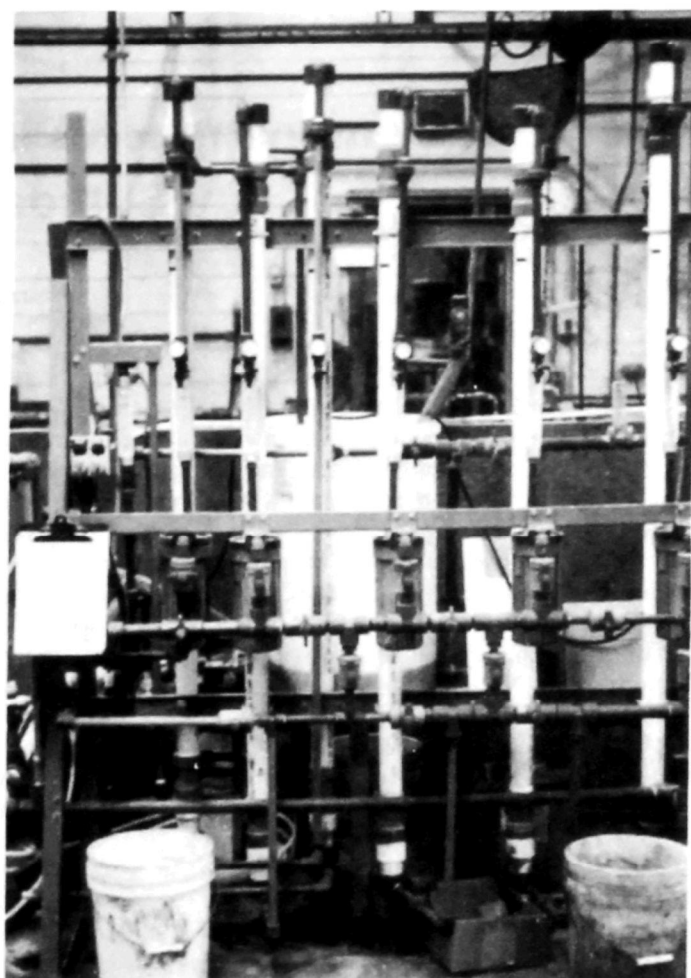
Fig. 11—Donnan Dialysis System on-site.

counterflow and parallel. Individual valves, pressure gages, flowmeters and filters control the flow through each tube. A photo of the completed unit undergoing hydraulic testing is shown in Figure 10. Pumps for feed and strip solutions are mounted at the rear of the unit. Installation on-site was completed only about two months ago. In operation, the first rinse of a counterflow sequence, currently averaging 0.5 g/l nickel, is recirculated through the tube-side of the modules and a 1-2 normal acid strip pumped through the shell side from a separate reservoir. Nickel-laden strip solution is to be used to replenish the plate tanks, as required, and the acid concentration renewed daily. Figure 11 is a view of the installed unit. The strip reservoir can be seen in the rear. Preliminary results are consistent with the laboratory tests in yielding a nickel transfer rate of about 2 g/hr/ft² depending chiefly on variation in rinse concentration.

After collecting preliminary data on the performance of the individual tubes and checking the several possible operating modes, the unit will be adjusted to optimize nickel recovery and minimize counterflow volume. The final results will be used to determine what type of recovery operation is best suited for Donnan dialysis and as a basis for design of a prototype commercial unit. One interesting concept is to use Donnan dialysis as the final step in a sequence of treatment processes to produce very low contaminant levels in the final effluent. Processes such as electrodialysis, which have relatively higher recovery rates and more concentrated products would do most of the reclaim work. In any event, Donnan dialysis seems certain to become a useful metal recovery and pollution control technique.

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An EPA Demonstration Plant For Heavy Metals Removal By Sulfide Precipitation

Murray C. Scott*

The Holley Carburetor Company, a Division of Colt Industries, Paris, Tennessee was awarded a grant by the EPA to demonstrate the effectiveness of a new approach to removal of heavy metals from waste streams by sulfide precipitation. The process, called Sulfex^{TN}, was developed by the Permutit Company. Before the process was demonstrated at Holley Carburetor, preliminary pilot plant work was done by the Permutit Company at their research facilities. The work was done under a grant made to the National Association of Metal Finishers by the EPA.

The surfaces of the carburetor castings are of either zinc or aluminum and are chemically treated according to finishing specifications established by the automotive industry. A "Udylite" automatic rack line dips the castings into various treatment and rinse water tanks according to a pre-arranged program. The water rinses following the treatment tanks are the source of contaminated wastewater which must be treated before discharge into the city of Paris sewer system. Figure No. 1 illustrates the automatic line. Rinse flow is on the order of 35 gpm.

There are three basic cycles of treatment: (1) zinc chromate, (2) deoxidize, (3) aluminum chromate. Composite samples of rinse water were collected during each cycle and analyzed. The analytical results obtained are shown in Table No. 1. For design purposes these concentrations were increased by 20% as a factor of safety.

Two metals, chromium and zinc, had to be removed before discharge of this waste into the city sewer. Total zinc was not to exceed 0.10 mg/l and total chromium was not to exceed 1.0 mg/l. These were the effluent limits prescribed by Holley Carburetor in their bid specifications. Whether conventional "lime and settle" would meet these effluent limitations was questionable, as shown by solubility curves for zinc and chromium hydroxides in Figure No. 2.

The amphoteric properties of metal hydroxides frequently make the results of the "lime and settle" approach questionable. An operating pH ideally suited for good removal of one metal causes another metal to go

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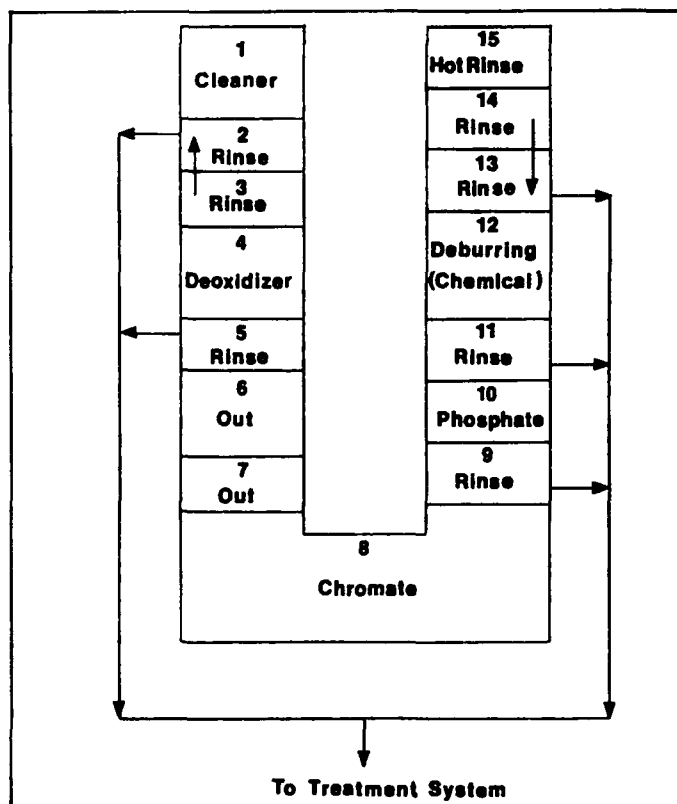
Fig. 1—Automatic line.

	TABLE I		
	PROCESS CYCLES		
	Zinc		*Aluminum*
	Dichromate	*Deoxidize*	*Chromate*
Ca	10 mg/l	8 mg/l.	9 mg/l
Mg	4	3	3
Na	50	39	37
K	3	3	3
Fe	1.4	1.7	1.1
Mn	0.02	0.03	0.10
Al	6	13	4
Cr	81	46	57
Zn	71	42	34
Ni	0.05	0.05	0.05
Cu	0.10	0.12	0.07
Pb	0.10	0.10	0.10
Alk	10	12	12
Cl	9	5	6
SO$_4$	40	18	37
SiO$_2$	11.3	11.3	10.7
P	65	58	38

Fig. 2

Fig. 3—Solubilities of Metal Hydroxides and Sulfides.

into solution. The solubility curves shown in Figure No. 2 suggest that the pH best suited for removal of zinc is about 10.0. At this pH (10.0) chromium has a solubility of about 5.0 mg/1, well above the maximum limit specified for this meal. The relationship of the solubilities of chromium and zinc shown in Figure No. 2 are used only to illustrate potential problems that might occur. These solubilities will vary with composition of the waste, but, the amphoteric properties of the precipitated metal hydroxides are forever present. However, if the heavy metals could be precipitated as sulfides, a mixture of metals would not be competing for optimum pH values. Comparison of the solubilities of various metal hydroxides and metal sulfides is shown in Figure No. 3. Not only are the metal sulfides not amphoteric, their solubilities are theoretically orders of magnitude below the metal hydroxides and decrease further with increasing pH.

THE SULFEX^{TN} PROCESS

The Sulfex process uses an insoluble salt as the source of the sulfide ion. Selection of the salt is not random. The solubility of the insoluble salt must be greater than the solubility of the heavy metal sulfide to be precipitated. As indicated in Table No. 2, ferrous sulfide is more soluble than the heavy metal sulfides that would be precipitated from metal finishing waste streams, so the Sulfex process uses ferrous sulfide as the source of sulfide ions.

Solubility products are taken from 11th edition of Lange's Handbook of Chemistry.

The iron sulfide works best when it is a freshly prepared slurry. For practical reasons, pulverized iron

TABLE II SOLUBILITY PRODUCTS

	Hydroxide	Sulfide
Iron	8.0×10^{-16}	6.3×10^{-18}
Zinc	1.2×10^{-17}	1.6×10^{-24}
Cadmium	2.5×10^{-14}	8.0×10^{-27}
Nickel	2.0×10^{-15}	3.2×10^{-19}
Copper	2.2×10^{-20}	6.3×10^{-36}
Lead	8.0×10^{-28}	1.2×10^{-15}
Mercury	3.0×10^{-26}	1.6×10^{-52}
Silver	2.0×10^{-8}	6.3×10^{-40}

sulfide is not used. Since only the surface of the large particle is useful, much of the iron sulfide particle would be wasted. However, freshly precipitated iron sulfide has a great deal of reactive surface. Quantities of iron sulfide required to adequately remove metals from waste streams will vary from 1.2 times stoichiometric to 3.0 times stoichiometric.

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Characteristics of the Sulfex[TM] process, when properly applied, offer a high degree of flexibility. Because of the low solubility of iron sulfide, the sulfide ion concentration is constantly maintained at about 0.02 ppb. Yet sufficient sulfide is available to accommodate wide variations in influent metal concentrations because the sludge blanket in the clarifier contains a large quantity of active iron sulfide. There is the additional asset of being able to reduce and remove hexavalent chromium in one step. The chemistry of the Sulfex process may be illustrated by two equations:

(1) $Cu(OH)_2 + FeS \rightarrow CuS + Fe(OH)_2$

(2) $Na_2CrO_4 + FeS + 4H_2O \rightarrow$
$\qquad Cr(OH)_3 + Fe(OH)_3 + 2NaOH + S$
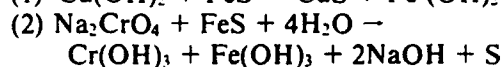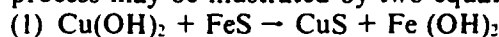
Because of the low concentration of sulfide ion, soluble sulfide complexes do not form with mercury, tin or silver as shown in the following equations:

$$HgS + S^= \rightarrow HgS_2^=$$
$$SnS_2 + S^= \rightarrow SnS_3^=$$
$$Ag + S^= \rightarrow AgS^-$$
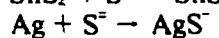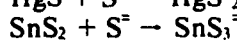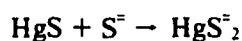
WASTE TREATMENT SYSTEM

The waste treatment system is designed to handle a maximum flow of 35 gpm. The operating day is 16 hours. A schematic of the system is shown in Figure No. 4. The treatment consists of neutralization, precipitation, clarification, filtration and sludge dewatering.

All rinse water comes into a two-compartment basin. The first compartment has a retention time of 105 minutes and the second compartment which normally operates with an average depth of 3 ft. has a detention time of about 80 minutes. The second compartment is operated at a low level so that it may accommodate filter backwash. These two holding compartments help equalize the waste but their primary function is to permit neutralization to a pH of about 8.5. Neutralization is done in two steps by the addition of lime which is controlled in both steps by pH sensing devices. The lime metering pump in the first step operates on-off. In the second step the lime metering pump has electronic stroke
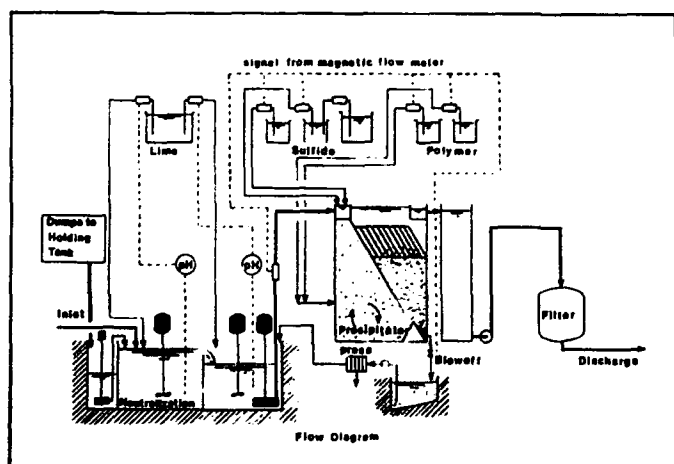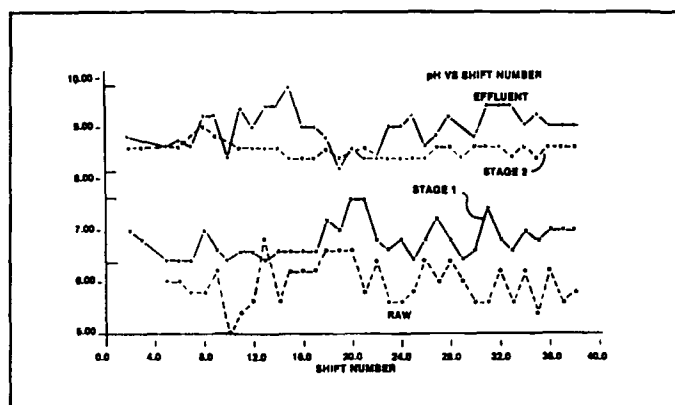
Fig. 5—Average pH Value of Raw Influent, Neutralization Stage I and II, and Precipitator Effluent as a Function of Time.

adjustment which is controlled by degree of deviation from the pH set point. Figure No. 5 shows comparative pH data for the raw waste, 1st stage neutralization, 2nd stage neutralization, and treatment plant effluent. The pH of the precipitator influent was closely controlled, ranging between a high of 9.0 and a low of 8.3; however, after the system was stabilized the pH was usually between 8.3 and 8.7. (The reduction of hexavalent chromium in the clarifier (precipitator) raised the pH and produced effluent pH values generally between 8.4 and 9.6).

Neutralized waste is then pumped to the clarifier where an iron sulfide slurry and a polymer are added. The rate of addition is proportional to influent flow. Jar tests are made twice each shift to determine the iron sulfide and polymer requirement. Timers on the panel board are then adjusted to change the cycle of the chemical feed pumps. The stroke of the pumps may also be changed, if desired, giving further flexibility to control of the chemical feeders.

The clarifier is a sludge blanket type, as illustrated in Figure No. 6. A slowly rotating mixer beneath the curtain baffle promotes floc formation. The floc mixture passes beneath the baffle into a section where the rise rate diminishes as the top of the unit is approached. This produces a blanket with a relatively sharp line of
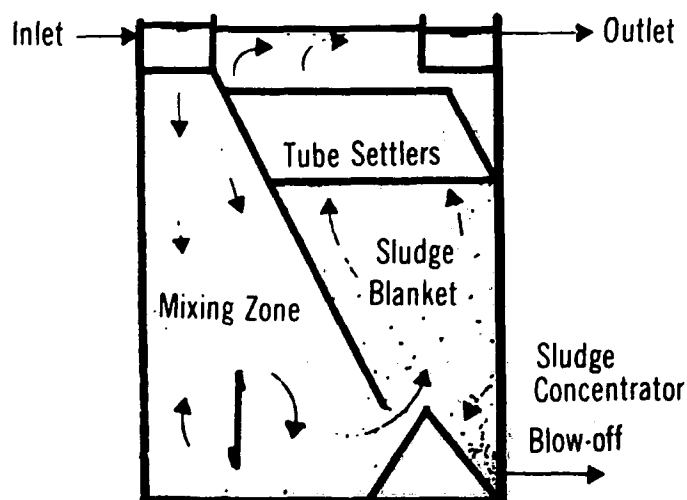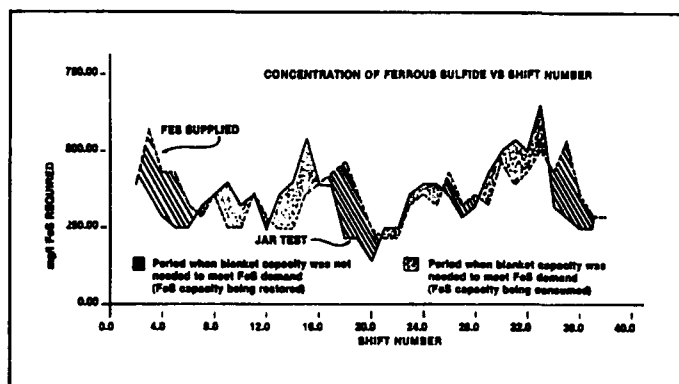

Fig. 4

Fig. 6

Fig. 7—Effect of Variable Ferrous Sulfide Requirement on the Reverse Ferrous Sulfide Capacity of the Sludge Blanket as a Function of Time.

Note: X's are points where no jar test was made.

demarcation between the top of the blanket and the clear water above the blanket. This blanket of suspended solids, which will range in concentration from 5000 mg/l to 15,000 mg/l, may consist of as much as 50% active iron sulfide. It is this reservoir of iron sulfide which allows the system to accommodate wide variations of influent metal concentrations with no change in the effluent quality.

To illustrate the effect of the iron sulfide reservoir in the sludge blanket, we ran jar tests on grab samples taken from the second neutralization basin to determine the amount of sulfide required. The yellow color of the chromate in the sample was used as an indicator. Source of the iron sulfide for this test was slurry taken from the chemical feed tank. When sufficient iron sulfide slurry has been added to react with all the metals and the hexavalent chromium in the sample, the yellow color disappears. The required iron sulfide dosage indicated by the jar test and the amount of iron sulfide being introduced by the chemical feed system at that time were noted and plotted on the graph shown in Figure No. 7.

Those areas with diagonal lines represent times when the actual feed of iron sulfide exceeded the demand, so active iron sulfide was accumulating in the sludge blanket. The dotted areas represent times when the actual demand from iron sulfide exceeded the feed rate, so active iron sulfide from the sludge blanket was being consumed. Total detention time of iron sulfide in the sludge blanket is about 19 hrs.

The amount of active iron sulfide in the sludge blanket
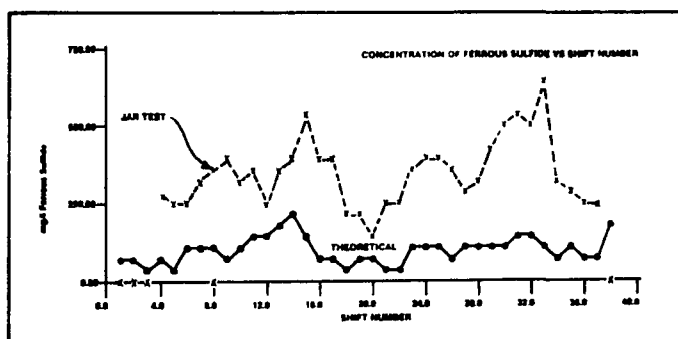
Fig. 8—Theoretical Ferrous Sulfide Requirement Compared with Jar Test Requirement as a function of Time.

Note: X's are points where no jar test was made.

can be controlled by adjusting the rate of feed of the iron sulfide slurry; however, excessive feed rates will increase chemical operating costs. For this reason, we were interested in stoichiometric iron sulfide requirements. The waste was analyzed for metals and then the stoichiometric sulfide requirement was obtained by calculation. A comparison of stoichiometric sulfide requirement and the sulfide requirement indicated by jar testing is shown in Figure No. 8. The jar test sulfide demand varied from 200% to 500% of the theoretical, averaging about 3.5 times stoichiometric. With more operating experience, closer control is expected to reduce the iron sulfide consumption.

The clarifier has a sludge concentrator which is blown off automatically, based on influent flow to the clarifier.

Since the amount of blowoff required is a function of both the hydraulic load and the suspended solids load, the blowoff rate is further controlled by adjusting a timer which determines the length of time the blowoff valve is open. This is estimated by collecting a sample from the unit to determine the height of the sludge blanket in the tube settlers. Two sampling points, one within the tube settlers and one six inches below the tube settlers, permits the operator to determine whether the blanket is too high or too low.

The blowoff is collected in a sump and then pumped through a filter press for dewatering. A polypropylene filter cloth is used. No precoat or body feed is required. Operation is at constant pump drive speed until the pressure builds up to 50 lbs. At this pressure, the resulting cake breaks away cleanly from the cloth. Down time is about 10-15 minutes. Operating time is about 10-14 hours. The unit holds slightly over 5 cu. ft. Dewatered cake is disposed at a local landfill.

The feed to the press contained from 14,000 mg/l to 24,000 mg/l suspended solids. Effluent from the press contained about 3 mg/l suspended solids at the beginning of the run and 22 mg/l at breakthrough (at end of run). Filter cake contained about 25% solids. On a total dry weight basis, the percentages of metals in the filter cake are shown in Table No. 3

The Sulfex process produces more sludge than a conventional "lime and settle" process, because a mole of insoluble ferrous hydroxide is produced for each mole of heavy metal sulfide formed. The excess iron sulfide in the clarifier sludge blanket also adds to sludge volume. This must be taken into consideration and adequate sludge disposal included as part of the overall design of the Sulfex treatment system. For example:

When designing a conventional rinse water waste

TABLE III	
Cr	3.3% to 4.5%
Fe	26.9% to 33.0%
Cu	<0.1%
Zn	3.7% to 4.1%
Total Solids	23.4% to 29.3%

treatment system, the waste is usually neutralized before clarification. The addition of iron sulfide to the clarifier converts this treatment system to the Sulfex[IN] process. This method of applying the Sulfex process results in a substantial increase in sludge production (on the order of 2.8 times) over straight lime treatment. It can only be justified where total metal concentrations are very low, or where there is inadequate space to permit a Sulfex polishing system.

A Sulfex polishing system uses a second clarifier. Iron sulfide and a polymer are added to this clarifier. Chemical requirements are quite low, since only residual metals from the hydroxide process need be treated. In applications of this type, the amount of additional sludge produced by the Sulfex process usually will amount to only 1% to 2% of the total sludge produced by the entire treatment system.

Supernatant from the clarifier is then pumped to a dual media, anthracite-sand, filter which is equipped with an air scour to insure good cleaning during the backwash procedure. Prudence, sound engineering, and requirement of a performance guarantee make filtration mandatory, but excellent quality is possible without filtration, as illustrated in Table No. 4.

TABLE IV

Metal	Clarifier Effluent mg/l	Filtered Effluent mg/l
Zn	0.1 to 0.5	≤ 0.05
Fe	0.3 to 4.0	≤ 0.50
Cu	≤ 0.01	≤ 0.01
Cr (Total)	0.1 to 1.0	≤ 0.04
Cr[+6]	≤ 0.05	≤ 0.04
Total Suspended Solids	1.0 to 10	≤ 0.5 - 1.0

Filtered effluent from the treatment system at Holley Carburetor routinely produced metal concentrations lower than detectable by today's accepted analytical methods. Metal concentrations in the influent and effluent are shown in Figures No.'s. 9, 10, 11, 12, 13.

Fig. 10—Average Concentration of Hexavalent Chrome in Raw Influent and Filter Effluent as a Function of Time.
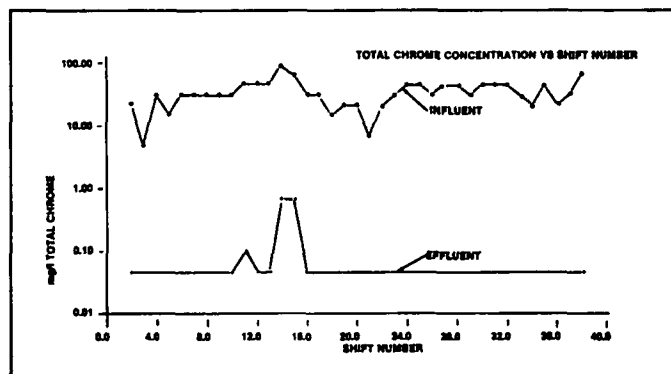
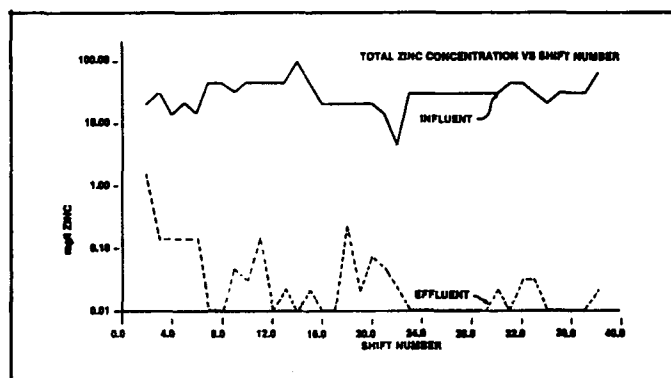Fig. 11—Average Concentration of Total Chromium in Raw Influent and Filter Effluent as a Function of Time.

Fig. 12—Average Concentration of Total Zinc in Raw Influent and Filter Effluent as a Function of Time.
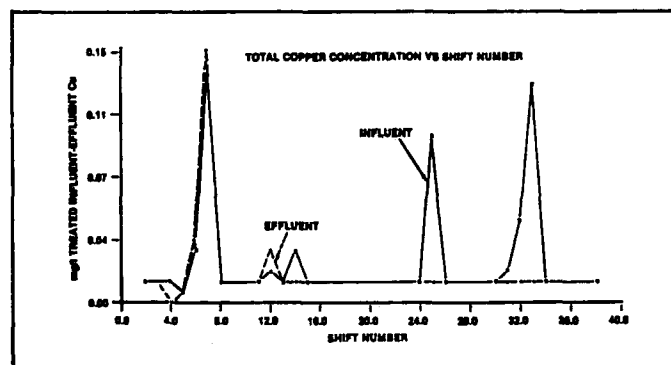

Fig. 9—Average Concentration of total Iron in Raw Influent and Filter Effluent as a Function of Time.

Fig. 13—Average Concentration of Total Copper in Raw Influent and Filter Effluent as a Function of Time.

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CHEMICAL OPERATING COSTS

Detailed data was collected over a period of 38 shifts (19 days). This included the startup period when all equipment was checked out and plant personnel were being trained. About 22 shifts (11 days) were required to reach a steady state where operating conditions were considered normal. For this reason only, data collected during the last 16 shifts (8 days) were used for calculating chemical operating costs. During this period, the flow averaged 26 gpm. Metal concentration averaged 34 mg/l Cr^{+6} and 34.7 mg/l Zn. The pH ranged between 5.2 and 6.5

Unit cost for chemicals were as follows:

Ferrous Sulfate	6.75¢/lb
Sodium Sulfhydrate	26.5¢/lb
Lime	4.65¢/lb
Polyelectrolyte	105.0/lb

The total chemical cost per shift is shown in Figure No. 14.

Comparison of the stoichiometric iron sulfide demand for zinc and hexavalent chromium can be used to give a chemical operating cost value to each. The total average chemical cost per shift was $18.50. The kilograms of dry solids produced per shift was 3.24 of which 1.6 kg contains chromium and 1.63 kg contains zinc.

$$\frac{\text{Stoichiometric FeS Requirement for } Cr^{+6}}{\text{Stoichiometric FeS Requirement for } Cr^{+6} + Zn} = Cr^{+6} \text{ fraction}$$

$$\frac{1.67 \text{ kg FeS/kg } Cr^{+6}}{3.01 \text{ kg FeS/kg } Cr^{+6} + Zn} = 0.555, Cr^{+6} \text{ fraction}$$

$$1.0 - 0.5548 = 0.4452, \text{ Zn fraction}$$

$$\frac{0.5548 \times \$18.50}{1.61 \text{ kg}} = \$6.38/\text{kg } Cr^{+6}$$

$$\frac{0.4452 \times \$18.50}{1.63} = \$5.05/\text{kg Zn}$$
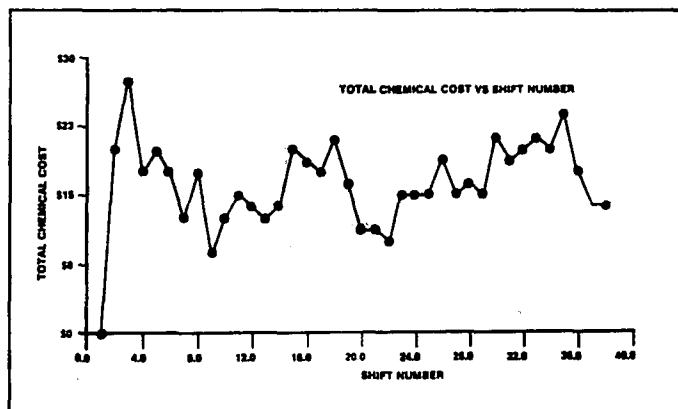
Fig. 14—Total Chemical Cost as a Function of Time.

COMPARATIVE CHEMICAL COSTS FOR CONVENTIONAL TREATMENT

Conventional treatment would consist of the addition of sulfuric acid to reduce the pH to 2.0, the addition of sodium bisulfite to reduce the chromium, followed by lime for neutralization and precipitation of the metal hydroxides. Unit costs for chemicals obtained locally are:

Bisulfite	23¢/lb	($0.5072/kg)
Sulfuric Acid	4.65¢/lb	($0.1025/kg)
Hydrated Lime	4.65¢/lb	($0.1025/kg)
Polyelectrolyte, anionic	225¢/lb	($4.96/kg)

The theoretical requirements to remove one kilogram of hexavalent chromium would be as follows:

(1) Bisulfite - 3 Kg $NaHSO_3$ is required to reduce 1 Kg Cr^{+6}. Since an excess of about 50% over stoichiometric is normally required, the amount of $NaHSO_3$ needed is:

$$3 \text{ Kg } NaHSO_4 \times 1.5 = 4.5 \text{ Kg } NaHSO_3/\text{kg } Cr^{+6}$$

(2) Sulfuric Acid - To acidify the waste water from pH 5.5 to 2.0 - 2.5 requires 516 mg/l 66° Be H_2SO_4, thus:

$$\frac{1 \text{ liter}}{34 \text{ mg } Cr^{+6}} \times \frac{10^6 \text{ mg}}{\text{kg}} = \frac{29,411 \text{ liters}}{\text{kg } Cr^{+6}}$$

$$\frac{29,411 \text{ liters}}{\text{kg } Cr^{+6}} \times \frac{5.16 \times 10^{-4} \text{ kg}}{1} = 15.18 \text{ kg/kg } Cr^{+6}$$

The stoichiometric requirement of H_2SO_4 for reduction of chromium is 1.42 kg H_2SO_4/Kg Cr^{+6}, therefore, the total acid requirement is:

$$15.18 \text{ kg} + 1.42 \text{ kg} = 16.6 \text{ kg/kg } Cr^{+6}$$

(3) The hydrated lime required to bring the pH back to 8.0 - 9.0 is 750 mg/l as Ca $(OH)_2$. Translating to kg/kg Cr^{+6}:

$$\frac{1 \text{ liter}}{34 \text{ mg } Cr^{+6}} \times \frac{10^6 \text{ mg}}{\text{kg}} = \frac{29,411 \text{ liters}}{\text{kg } Cr^{+6}}$$

$$\frac{29,411 \text{ liters}}{\text{kg } Cr^{+6}} \times \frac{7.5 \times 10^{-4} \text{ kg}}{1} = 22 \text{ kg/kg } Cr^{+6}$$

(4) Polyelectrolyte - Anionic polyacrylamide polymers are frequently used at dosages of about 1 mg/l, thus:

$$\frac{29,411 \text{ liters}}{\text{kg } Cr^{+6}} \times \frac{1.0 \times 10^{-6} \text{ kg}}{1} = 0.03 \text{ kg/kg } Cr^{+6}$$

Summarizing the chemical costs:

Bisulfite	= 4.5 kg × $0.507	= $2.28/kg Cr^{+6}
Sulfuric Acid	= 16.6 kg × $0.103	= $1.71/kg Cr^{+6}
Hydrated Lime	= 22 kg × $0.103	= $2.27/kg Cr^{+6}
Polyelectrolyte	= 0.03 kg × $4.96	= $0.15/kg Cr^{+6}
Total Chemical Cost		= $6.41/kg Cr^{+6}

Comparing the chemical costs for treatment of this waste by conventional methods with chemical costs for treatment by the Sulfex process is difficult, but the following data is a reasonable estimate:

TABLE V			
	Conventional	Primary Sulfex	Polishing Sulfex
For Chromium	$6.41 kg	$6.38/kg	$6.39/kg
For Zinc	0.17/kg	5.05/kg	.17/kg
For Sludge Disposal	1.16	2.32	1.88
Total	$7.74	$13.75	$8.44

With this particular waste, a portion of the sludge comes from precipitation of phosphate. Unfortunately, we did not collect detailed analytical data on phosphate concentrations because removal of phosphate was not required. The original analytical data showed a low phosphate concentration of 38 mg/l as P and a high of 65 mg/l as P. The low concentration was used for estimating the sludge produced by phosphate precipitation and the value was included in the assessment of comparative sludge disposal costs.

Increased chemical usage and increased sludge is the premium paid for primary Sulfex treatment where the FeS is added to the same clarifier that would be used for conventional hydroxide precipitation. The third column in Table No. 4 shows costs for chemicals and sludge disposal for a complete treatment system which includes polishing by the Sulfex process.

COST ANALYSIS

Operating Costs

The yearly operating cost, excluding depreciation and licensing fees, for the treatment system at Holley Carburetor is outlined below. This cost results from charges incurred by operators, utilities and chemicals.

The estimated yearly operating cost, based on plant performance to date, is as follows:

1. Operators Salaries:

$10,800 per operator × 2 operators = $21,600
+ fringe benefits at 40% = 8,640

Total Salaries = $30,240/year

2. Electricity:

$$\frac{203.32\,kwh}{day} \times \frac{5\,day}{wk.} \times \frac{52\,wk.}{yr.} \times \frac{\$0.0191}{kwh} = \$1010/year$$

3. Water:

4162 m³ × $0.053/m³ = $220/year

4. Chemical:

$$\frac{\$14.69}{shift} \times \frac{2\,shifts}{day} \times \frac{260\,days}{yr.} = \$7639/year$$

5. Sludge Handling and Disposal Cost:

$$\frac{\$15}{day} \times \frac{260\,days}{yr.} = \$3900/year$$

Total Operating Cost is therefore:

Salaries	=	$30,240
+ Electricity	=	1,010
+ Water	=	220
+ Chemicals	=	7,639
+ Sludge Disposal	=	3,900
TOTAL		$43,009/year

Capital costs are itemized as follows:

Equipment	$92,465
Engineering Costs (Consulting, report to state and design for underground tanks)	17,400
Underground Tanks	48,000
Shipping and Installation	21,730
Taxes (on equipment only)	1,089
	$180,684

SUMMARY

Precipitation of heavy metals by sulfide will in most cases permit any plant to economically meet extremely rigid discharge standards but frequent complaints are lodged that disposal of sulfide sludges presents a serious impediment to acceptance of any sulfide process for heavy metals removal. The complaints are not necessarily on solid ground.

In almost all cases the waste streams are neutralized with lime or caustic. This results in the precipitation of metal hydroxides. The next logical step is to remove these precipitated metals by coagulation and settling or any other technique that might be applicable. Sulfide precipitation, if required, should be applied to residual soluble metals which represent a very small portion of the total metals originally present in the waste streams. Is there any reason why this very small sludge portion consisting of metal sulfides cannot be disposed in the same manner as the large portion of metal hydroxides?

The leaching test procedure, described in the Dec. 18, 1978 Federal Register, page 58596, was used to obtain the following comparative data on a sludge produced by the Sulfex process and on a sludge produced by the addition

of lime. A solution containing 20 mg/l of each metal was used for the test. Equal portions of this solution were treated, one by Sulfex^{TN} and the other by lime. The sludge produced by each procedure was then subjected to the leaching test recommended by the EPA. The pH of the Sulfex mixture was 5.7. The pH of the hydroxide mixture was 5.8.

The Sulfex mixture gave no odor of H_2S nor was there any evidence of H_2S detectable by lead acetate paper.

EXTRACT LEVEL mg/l			
	EPA Proposed Regulation	Sulfex	Hydroxide
Arsenic	0.50	—	—
Barium	10.0	—	—
Cadmium	0.10	0.02	1000
Chromium (Total)	0.50	< 0.05	1.5
Lead	0.50	0.20	55
Mercury	0.02	—	—
Selenium	0.10	·	
Silver	0.50	0.02	0.21
MAY BE CONSIDERED IN FUTURE			
Ni	—	35	>33
Fe	3	820	< 1
Zn	50	0.36	1475
Cu	10	0.03	259

These data would suggest that disposal of sulfide sludges will present no more of a problem than disposal of hydroxide sludges. Both appear to be material that should be disposed in a secure landfill.

The Development of an Activated Carbon Process For the Treatment of Chromium (VI)— Containing Plating Wastewater

C. P. Huang & A. R. Bowers*

INTRODUCTION

Ever since Ostrejko[1] discovered in 1900 that, when treated with mineral chloride, vegetable charcoal exhibits decoloring power 10 times greater than untreated charcoal, many brands of activated carbon have been manufactured and used by various industries.[2,3] Early applications of activated carbon were associated mainly with material production, such as sugar refining, oil and drug purification. Use of activated carbon for water treatment in the United States was first reported in 1930, for the elimination of taste and odor.[4] Due, in part, to this historical connection, most of the applications of and research effort on activated carbon in the water and wastewater industries are oriented toward organics removal. Research efforts on inorganics removal by activated carbon, specifically metallic ions, are markedly limited.

This paper presents some of the most recent developments concerning applications of activated carbon for total chromium removal.

Recently, the removal of inorganic pollutants and heavy metals by activated carbon adsorption has received considerable attention. Much of this work has been done in Japan, where heavy metals are a pressing concern. Kawashima and others reported significant removal of heavy metals from synthetic wastewaters using activated charcoal.[5] Saito showed that the removal of heavy metals such as copper, cadmium and ferric iron could be improved by treating activated carbon with sulfonate.[6] Huang and Ostovic found a variety of commercial activated carbons to effectively adsorb cadmium, Cd(II), from dilute aqueous solution, largely as a result of charge development on the carbon surface.[7]

Use of activated carbon to remove chromium (VI) from water is a recent endeavor. Toyokichi reported that[8] chromates are effectively removed by passing wastewater containing chromates through a column packed with platinum black catalyst-impregnated activated carbon.

One kg of activated carbon was mixed with 1 ml platinum black colloid containing 0.001 mg Pt/l and 1 g pure H_2SO_4. The platinum black catalyst-impregnated activated carbon (50 l) was packed in a column, then wastewater containing 100 ppm of chromate was passed through the column at 1 m^3/hr. The resulting wastewater contained less than 0.1 ppm of chromate. Similar research was conducted by Tagashira, et al.,[9] who found that mixing 200 ml $K_2Cr_2O_7$ solution (534 ppm Cr) with 5 g powder coconut shell charcoal (100-200 mesh 15%, 200-325 mesh 15% and <325 mesh 70%) and heating in an autoclave at 200° C for 30 minutes can reduce the Cr(VI) concentration to 0.01 ppm.

Huang and Wu[10] studied the removal of chromium(VI) by calcinated charcoal and found that removal was most significant at low pH and low initial Cr(VI) concentration, they also postulated that $HCrO_4^-$ ions are the major species being removed.

Seto and Tsuda[11] reported that by mixing a 50-ml Na_2CrO_4 (10%) solution, with 5 g activated carbon in a flask for 2 hrs at 25° C, the CrO_3 adsorption by the activated carbon was 38.7% and 3.3%, respectively, when the pH was 3 and 7.

By heating lignite with 14% HNO_3 acid for 13 minutes, Nagasaki[12] demonstrated that chromic acid ions were effectively removed. By passing a wastewater containing chromic acid (100 ppm), with pH being adjusted to equal to or lower than that of chromic acid, through an activated carbon column for 100 hrs, Nagasaki and Terada[13] reported that the effluent contained neither Cr(VI) nor Cr(III). After treating 1350 l of wastewater, the effluent pH went up to 7 and contained 0.5 ppm Cr(VI). Ten liters of 25% HCl solution were then passed through the column to regenerate the column by dissolving the reduced Cr(III). The column was reused for another 100 hrs without breakthrough.

A Dutch process for reducing Cr^{+6} to Cr^{+3} with activated carbon was proposed by Roersma, et al.[14] An EPA-supported work conducted by Landrigan and Hallowell[15] also demonstrated that activated carbon can be used by many small plating plants to remove their chromium to relieve the burden on municipal sewage systems.

Yoshida, et al.,[16] studied the adsorption of Cr(VI) and Cr(III) onto activated carbon as a function of pH and the

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amount of total Cr and Cr (VI) eluted from activated carbon at pH 4 - 6.5. They reported that Cr(VI) is readily adsorbed on activated carbon as anionic species such as $HCrO_4^-$ and CrO_4^{-2}, while Cr^{+3} ion is scarcely adsorbed on activated carbon. They also observed that in acidic solution, Cr(VI) is easily reduced to Cr(III) in the presence of activated carbon. The adsorbed Cr(VI) species was elutable with NaOH (>0.1 N) or with 1 N HCl solution.

Huang and Wu[17] studied the effect of pH on Cr(VI) and Cr(III) adsorption by Filtrasorb 400 activated carbon.

It is evident that Cr(VI) can be readily reduced to Cr(III) at acidic condition and in the presence of activated carbon. Kim[18] reported that the reduction reaction can be suppressed by adjusting the proton concentration (i.e., H^+ ions) to become equal to that of the hexavalent chromate, or to maintain a Cr(VI) system predominated by $HCrO_4^-$ species. Although a similar statement has been made by Nagasaki and Terada,[13] no such finding was observed in a recent and more detailed study conducted by Huang and Bowers.[19]

INTERACTIONS OF CR(VI) WITH ACTIVATED CARBON

The removal of Cr(VI) from solution occurs through several steps of interfacial reactions: 1) the direct adsorption of Cr(VI) onto the carbon surface; 2) the reduction of Cr(VI) species to Cr(III) by carbon on the surface; and 3) adsorption of the Cr(III) species produced, which occurs to a much lesser extent than the adsorption of the Cr(VI) species. The rate of each reaction depends on the following mechanisms: a) the transport of Cr(VI) anions, $HCrO_4^-$, by molecular or eddy diffusion, toward the carbon surface; b) chemical reactions, reduction and/or adsorption, which take place on the external carbon surface; c) desorption and back transport of the Cr(VI) and Cr(III) species from the external surface into the bulk phase; d) inner transport of the Cr(VI) and Cr(III) species into the internal surfaces bounding the micropores and capillaries of the carbon; e) chemical reactions, reduction and/or adsorption, taking place at the internal surfaces; and f) back transport of the Cr(VI) and Cr(III) species across the internal surface and the external interface into the bulk phase.

Batch Experimental Cr(VI) Adsorption

Huang and Bowers[20] have conducted batch experiments on the kinetics of Cr(VI) removal of Filtrasorb 400 activated carbon. They found that reduction and adsorption occurred simultaneously and the kinetic equations were:

(1)

$$-\left(\frac{dCr(VI)}{dt}\right)_{red} = \frac{2.4[HCrO_4^-][C]\,G[H^+]}{1.2+4.8\times10^4[Cr(III)]+2.4\times10^5\,G[H^+][Cr(VI)]}$$

which is the rate of Cr(VI) reduction and:

$$\left(\frac{dCr(VI)}{dt}\right)_{ads} = 2.9\times10^{-2}\,[H^+]^{0.2}\,[C]\,[Cr(VI)]\left\{1-\frac{\Gamma}{\Gamma_e}\right\} \quad (1a)$$

which is the rate of Cr(VI) adsorption:

where the determining variables are as follows:

[C] = concentration of Filtrasorb 400 in the reactor (g/l)

$[HCrO_4^-]$ = concentration of bichromate (M)

[Cr(VI)] = concentration of total Cr(VI) species (M)

[Cr(III)] = concentration of soluble Cr^{+3} cations (M)

$[H^+]$ = concentration of protons in solution (M)

G = average velocity gradients in the reactor (sec^{-1})

Γ = the instantaneous adsorption density of Cr(VI) on the carbon surface (μ mole/g)

Γ_e = the adsorption density of Cr(VI) at equilibrium with the surface and liquid phases.

Batch experiments also showed that the maximum Cr(VI) adsorptive capacity of the carbon occurred at pH 2.5 and decreased rapidly between pH 2.5 and 7.1, primarily due to the decreasing electrostatic attraction between the postively charged carbon surface and the anionic Cr(VI) species in solution. The Cr(VI) adsorptive capacity decreased at pH < 2.5 due to the rapid reduction of the Cr(VI) species and the subsequent dominance of the cationic Cr(III) species at low pH.

Based upon these reaction Equations (1 and 1a), it is possible to eliminate Cr(III) production to achieve total Cr(VI) removal with a batch reactor.

Experiments with Packed Columns

Loosely packed carbon columns were run to determine the importance of the various operational parameters in maintaining an efficient and effective system for removal of Cr(VI) and to minimize the amount of Cr(III) produced.

The effects of carbon bed depth, influent Cr(VI) concentration, and pH on the removal efficiency were studied. Pre-washing of the carbon before contact with Cr(VI) was also investigated.

The influence of bed size on the removal efficiency is indicated in Figure 1 (a through d) for 10, 30 and 50 gram carbon beds, all receiving a constant influent of 2 gal/min/ft^2 or 44 ml/min, at pH 2.50, 10^{-3} M Na$_2$CrO$_4$ (52 ppm as Cr) and 0.1 M NaCl for ionic strength. The inability of the carbon to remove all of the Cr(VI) over the first few bed volumes, Figure 1 (a), is due to the high initial pH observed, primarily due to the amount of H^+ ions needed to hydrolyze the carbon surface. Since there is no Cr(VI) present after 100 bed volumes for 30 or 50 gram beds, Figure 1 (c), indicates that adsorption of the trivalent species does not occur and may be neglected.

The influent Cr(VI) concentration was varied from 1 × 10^{-4} M to 5 × 10^{-3} M Na$_2$CrO$_4$, 5.2 to 260 ppm as Cr, while the carbon bed size, influent pH, and flow rate remained constant, 50 g, 2.50, and 2 gal/min/ft^2, respectively. The results of these experiments are shown in Figure 2 (a through d). Figure 2 (a) shows a retardant effect of increased Cr(VI) concentration on the time required for
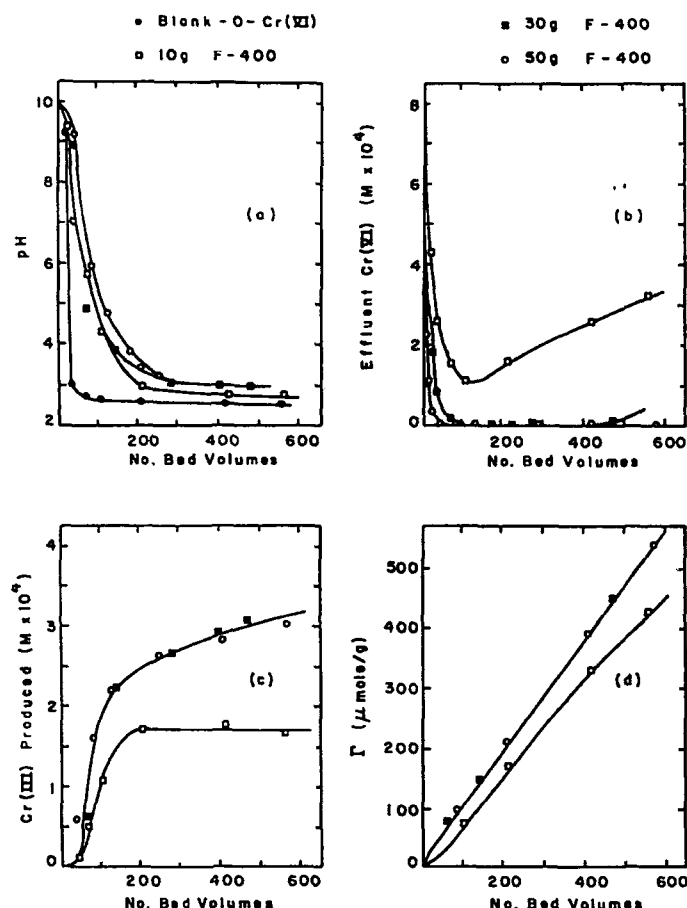
Fig. 1—The effect of carbon bed size on: a. pH, b. residual Cr(VI), c. Cr(III) produced, and d. the Cr(VI) adsorption density.
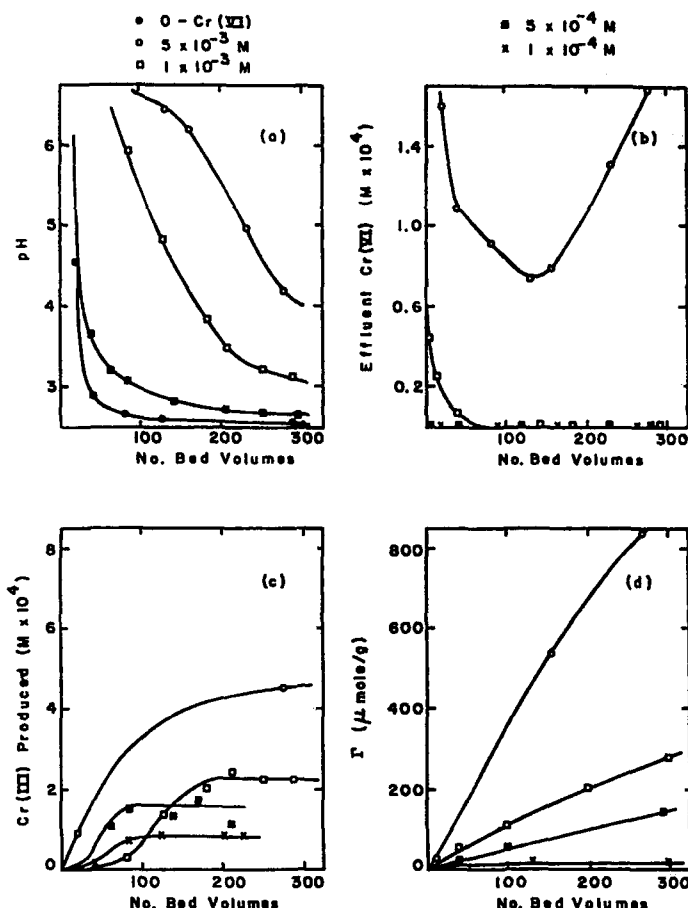

Fig. 2—The effect of increasing Cr(VI) concentration in the influent to a constant bed size (50g) on: a. pH, b. residual Cr(VI), c. Cr(III) produced, and d. the Cr(VI) adsorption density.

the pH of the column to equilibrate as the surface hydrolysis reactions go to completion. This is due to the increased demand imposed on the H^+ concentration as the influent Cr(VI) concentration is increased and more Cr(III) is subsequently produced, Figure 2 (c), and more Cr(VI) is adsorbed, Figure 2 (d).

The removal of Cr(VI) is incomplete for the initial bed volumes, Figure 2 (b), due to the high pH which is maintained for the first 100 bed volumes as a result of the H^+ demand for the hydrolysis reactions. The complete removal of 5×10^{-3} M Cr(VI) was never achieved during the entire experiment, since the pH remained high (greater than 4 over the entire 300 bed volumes). The H^+ concentration was insufficient to obtain complete removal. Also, the results of Figure 2 (c) show that Cr(III) will still be produced when the influent Cr(VI) to H^+ ratio is greater than one (1.58 for 5×10^{-3} M Cr(VI) to pH 2.50). The 1:1 ratio only applies generally, when the Cr(VI) concentration is less than 1×10^{-4} M or when a 1:1 ratio implies the pH is greater than 4.0, which is not a strong reducing condition regardless of the Cr(VI) concentration. Equation (1a) shows the reduction rate to depend on the first power of the H^+ concentration. This finding did not agree with what was reported by Kim and Zoltek,[18] who claimed a 1:1 total Cr(VI) to H^+ for minimum reduction and maximum adsorption reactions.

To eliminate the initial Cr(VI) removal deficiency and smooth out the pH in the system, the carbon must be pre-washed with an acidic solution before contact with Cr(VI). It is not recommended that a strong acid solution be used for this wash cycle, since strong acids are corrosive to the carbon and may result in a degree of hydrolysis which overshoots the equilibrium that can be obtained by the H^+ concentration in the subsequent wastewater influent. Therefore, the carbon must be hydrolyzed by a wash solution which closely approximates the pH of the influent to be treated. In a column configuration, the wash cycle may be accomplished in approximately 150 bed volumes or less, by a pH of 2.50 or less, while at pH 3.00 or greater the wash cycle requires too much time and becomes a cumbersome operation. In this case it may be more convenient to eliminate the concentration gradients which occur in a packed column and hydrolyze the carbon granules by titrating them with acid in a well-mixed reactor until an equilibrium pH is obtained, before placing the carbon into the column.

The results of pre-washing with 150 bed volumes of pH 2.50, 0.1 M NaCl washwater before contacting the carbon with Cr(VI) are shown in Figures 3 and 4 for 50 grams of carbon, 5×10^{-4} M and 1×10^{-3} M Na$_2$CrO$_4$, respectively, in the influent. The pH is observed to be
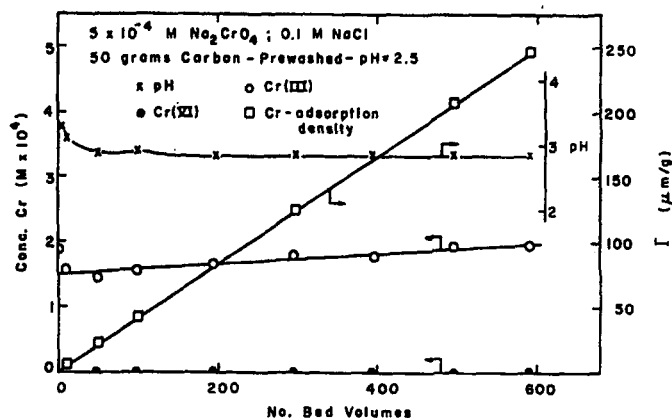
Fig. 3—The effluent characteristics of a 5 × 10⁻⁴ M Na₂CrO₄ (26 ppm Cr(VI)) wastewater after treatment with a pre-washed packed column.
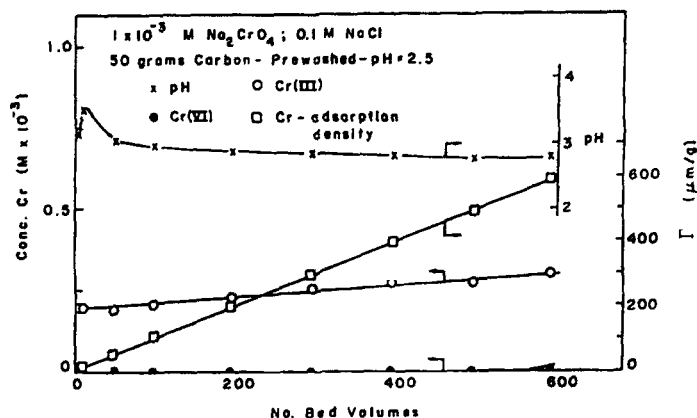

Fig. 4—The effluent characteristics of a 1 × 10⁻³ M Na₂CrO₄ (52 ppm Cr(VI)) wastewater after treatment with a pre-washed column.

much smoother over the course of operation and no Cr(VI) was detected in the effluent for 600 bed volumes. The production of Cr(III) was also consistent and increased linearly as the adsorption equilibrium and the progressive increase in Cr(VI) concentration propagated up the column.

Operation of Packed Column

Reduction of the Cr(VI) species cannot be eliminated from a packed carbon column, but a packed column is the most economical and simplest treatment scheme to operate. Therefore, if a separate carbon system can be devised to remove the Cr(III) produced, packed carbon columns would be an efficient, simple, economical and environmentally compatable treatment process for the removal of hexavalent chromium species from wastewater.

Column operation is sensitive to the pH in the wastewater influent stream since there is a stoichiometric requirement of 1 mole of H^+ per mole Cr(VI) adsorbed and 4 moles of H^+ per mole Cr(VI) reduced. In order to completely remove all of the Cr(VI) from solution, a 1:1 molar ratio of H^+ to Cr(VI) would be the absolute minimum ration of H^+:Cr(VI), if Cr(VI) was removed exclusively by adsorption. In fact, an excess of H^+ is required to satisfy the stoichiometric demand of H^+ for reduction and to prevent the decreased H^+ concentration in the latter portions of the column from limiting the removal rates and the Cr(VI) adsorptive capacity of the carbon.

For a case study, treating 10,000 gal of wastewater per day with 1×10^{-3} M Cr(VI) (or 52 ppm Cr), the maximum pH in the influent would be 3.0. However, an excess of H^+ is desired and the maximum Cr(VI) adsorptive capacity of the carbon occurs at pH 2.50 (70 mg Cr(VI)/g). Bench scale experiments have also indicated excellent Cr(VI) removal performance at this pH value.[20] Therefore, pH 2.50 appears to be the optimum condition for complete removal of Cr(VI) by adsorption and reduction.

The surface loading rate of the carbon columns in this study was 2 gal/min/ft². Therefore, at a wastewater flow rate of 10,000 gal/day operating 8 hr/day, the column would require 10.4 ft² of surface area or be 3.64 ft in diameter.

The depth of the column can be estimated from experimental data. Table I shows the experimental bed size and the number of influent bed volumes passed through each column before breakthrough occurred.

A log-log plot of bed volumes vs bed depth is shown in Figure 5. The number of bed volumes may then be written as a function of bed depth or:

$$\log (BV_b) = 0.92 \log (d_b) + 2.94 \qquad (2)$$

where BV_b = number of bed volumes to breakthrough

d_b = carbon bed depth (ft)

The depth of the bed can be evaluated by choosing the desired time interval between regenerations, which implies:

$$BV_b = \frac{7.48\ Q\ t}{(S.A.)\ d_b}$$

where: Q = wastewater flow rate (gal/day)
t = time interval between regenerations (days of actual system operation)
S.A. = column surface area perpendicular to the flow (ft²)

Q, t and S.A. should all be known, from which d_b can be derived by solving Equation (2). By assuming 10,000 gal/day with regeneration cycles once a month (22 days of actual operation), $d_b = 2.4$ ft. Therefore, a 4 ft diameter by 3 ft depth carbon bed would be a conservative design

TABLE 1

Column depth versus number of bed volumes to Cr(VI) breakthrough[a]

bed size (grams)	bed depth (ft)	no. of bed volumes to breakthrough
10	0.70	125
30	0.42	400
50	0.14	600

[a] flow rate = 2 gal/min/ft²; pH = 2.5; total Cr(VI) = 1×10^{-3} M

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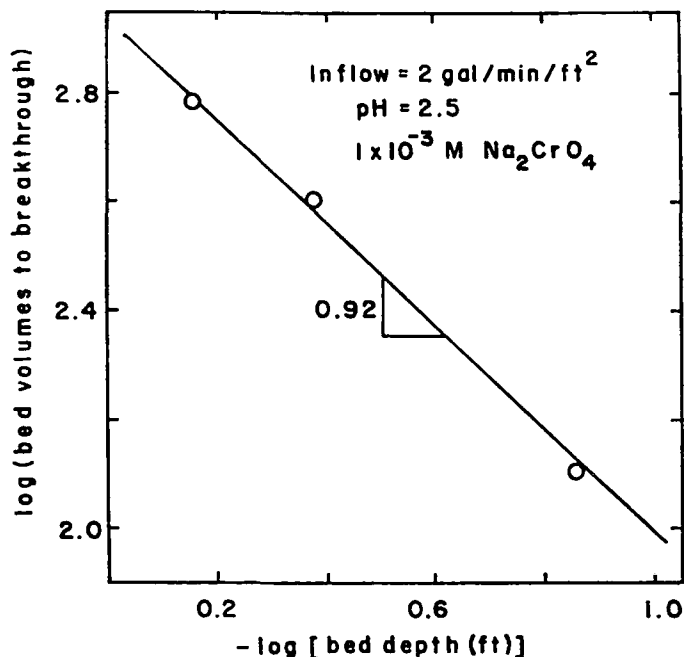
Fig. 5—Bed volume to breakthrough as a function of carbon bed depth for 1 × 10⁻³ M Na₂CrO₄ at pH 2.50.

Fig. 6—A comparison of Cr(VI) removal capacities following various regeneration techniques.

and require 1,082 lbs of carbon @ 61¢/lb. Thus, regenerating once a month at a 2% carbon loss means the operating cost for carbon for the column would be 0.01¢/gal.
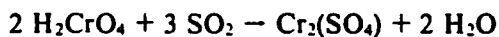
The initial column must be followed by a Cr(III) treatment system capable of treating 10,000 gal/day at 2.0 to 3.0 × 10⁻⁴ M Cr(III) (10 ~ 15 ppm).

It is also relevant to compare the cost of using activated carbon for Cr(VI) reduction to the cost of conventional reduction with sulfur dioxide (SO₂). The following unit material costs can be attributed to each:

Filtrasorb 400 costs 61¢/lb or $61/100 lb
SO₂ costs $8.51/100 lb

From the stoichiometry of the reduction reactions:

1. for Cr(VI) reduction by carbon, 3 moles of carbon are required to reduce 4 moles of Cr(VI)
2. for Cr(VI) reduction by SO₂ the following stoichiometry applies:

$$2\ H_2CrO_4 + 3\ SO_2 \rightarrow Cr_2(SO_4) + 2\ H_2O$$

or 3 moles of SO₂ is required per 2 moles of Cr(VI) reduced.

Therefore, assuming 100% efficiency of reaction, for 10,000 gal of 1 × 10⁻³ M (or 52 ppm as Cr) Na₂CrO₄ per day, to completely reduce all of the Cr(VI), the chemical costs would be 51¢/day for SO₂ and 46¢/day for Filtrasorb 400. Therefore, this concludes that it is favorable to use activated carbon as a reducing agent for conversion of Cr(VI) to Cr(III).

REGENERATION OF EXHAUSTED ACTIVATED CARBON

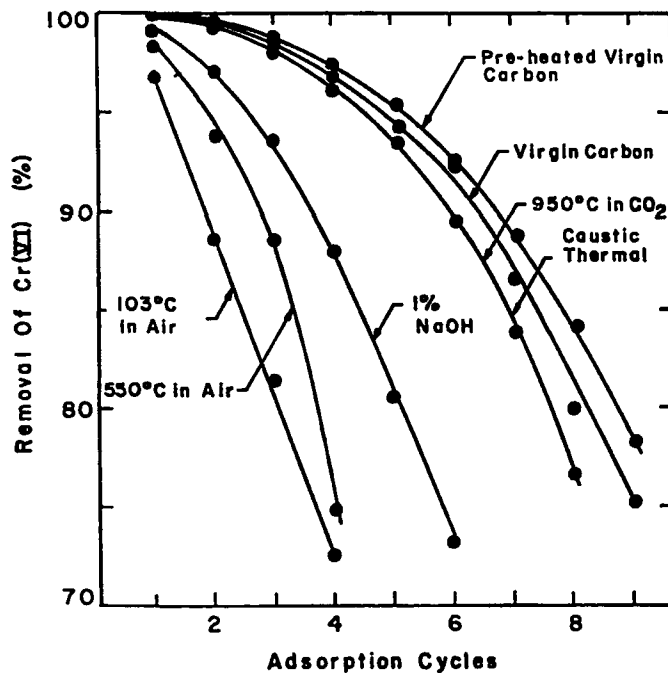If a full-scale system for the removal of Cr(VI) by activated carbon is to be practical or economically feasible, a sound regeneration procedure must be established. Regeneration must perform several functions and meet the following criteria:

1. The removal capacity must not be destroyed by the regeneration process.
2. Chromium must be removed from the carbon surface and concentrated in such a way that the resulting regenerant stream is much more concentrated than the original wastewater stream which was treated.
3. The carbon loss during regeneration must be minimal.
4. The process must be economically feasible.
5. The process should yield no secondary contaminants.

Four methods of regenerating the chromium-laden activated carbon were examined:

1. Thermal regeneration (drying at 103° C in air, 550° C in air or 950° C in CO₂).
2. Caustic regeneration (with NaOH).
3. Combined caustic-thermal regeneration (caustic and 950° C in CO₂).
4. Acid regeneration.

Restoration of Removal Capacity

In the first set of experiments, the carbon was exhausted by subjecting it to 9 successive batch adsorption cycles, after which the carbon was regenerated and the adsorption cycles repeated. Figure 6 shows the results for the removal of Cr(VI) after regeneration by treating with 1% NaOH, heating in air at 103° C for 24 hours or 550° C for one-half hour and heating at 950° C in CO₂ for one-half hour, compared with the virgin carbon and a virgin carbon pre-heated at 950° C in CO₂ for one-half hour. Thermal regeneration at 950° C, or the combined caustic-thermal techniques, show the same removal capacity and appear to be the
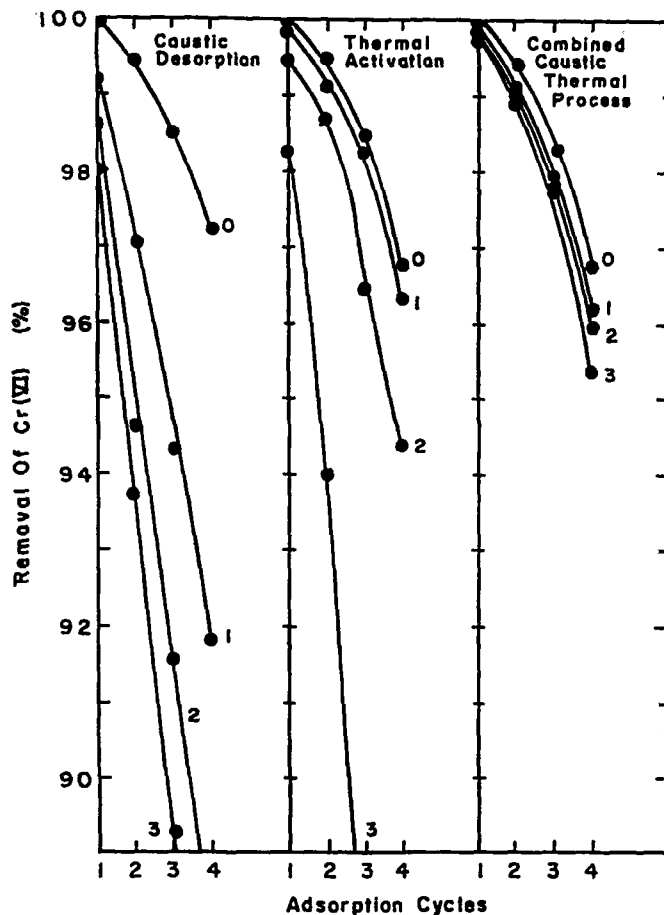
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Fig. 7—A comparison of regeneration techniques after 4 adsorption cycles and successive regeneration cycles.

TABLE 2

Average loss of carbon
during batch adsorption and regeneration cycles

Type of Operation	Average Loss of Carbon per Cycle, % by Weight
First adsorption cycle	0.17
Further adsorption cycles	0.06
Caustic regeneration cycle (1% NaOH)	1.50
Thermal regeneration cycle at 550° C in air	7.40
Thermal regeneration cycle at 950° C in CO_2	5.00

1. Thermal regeneration at 950° C in CO_2 results in a 5% loss of carbon, which translates into significant costs to supply the lost carbon.
2. The costs of building and operating a multiple hearth or fluidized bed furnace at 950° C for regeneration are prohibitive, except on a very large scale.
3. The resulting air pollutants, chrome carbonyl or other organo-chromium compounds, which are formed at high temperatures would require a great deal of additional study and undoubtedly require stringent controls which could be economically and technologically unfeasible.

Therefore, thermal techniques for regeneration of carbons laden with chromium cannot be an environmentally compatible or economically sound procedure.

Caustic Desorption of Adsorbed Chromium

The desorption of chromium from the carbon surface by treatment with caustic solution can be measured directly from chromium analysis of the wastewater treated and the regenerant solution used. Figure 7 shows the percent of chromium desorbed from the carbon surface by various NaOH solutions after successive 24 hour regeneration contact periods with the carbon. Ten grams of carbon were used, which was brought close to equilibrium in a packed column after 1300 bed volumes of influent, 1×10^{-1} M Na_2CrO_4, pH 2.50 and 0.1 M NaCl, which is equivalent to an adsorption density of *ca* 940 μm/g (5 mg Cr/g). The carbon was then regenerated in 500 ml of NaOH solution at the indicated strength.

From Figure 8, chromium is seen to be more effectively desorbed from the carbon surface as the strength of the caustic solution is increased, but the weaker solutions approach the efficiency of the stronger solutions as the number of regeneration cycles are increased. Therefore, the concentration ratio between chromium in the bulk solution and on the carbon surface increases with the caustic strength. Figure 9 shows the Cr(VI) concentrations reached in the bulk solution for the various caustic solutions during the regeneration cycles.
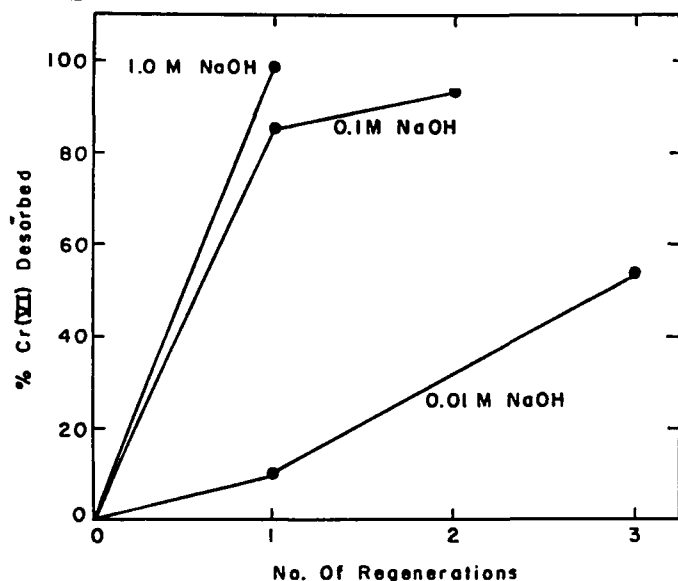
most effective, while 1% NaOH is next best, and drying in air at 103° C or 550° C appear to create little readsorption capacity. A comparison of the caustic, thermal (950° C in CO_2) and combined caustic-thermal regeneration techniques over several regeneration cycles is shown in Figure 7. Here the combined caustic-thermal technique acquires an advantage over the thermal regeneration alone, and the thermal regeneration approaches the same readsorptive capacity as caustic regeneration, as subsequent regeneration cycles are performed.

Loss of Carbon

The loss of original carbon due to various physical-chemical reactions is shown in Table 2.

The average loss of 0.17% carbon by weight during the first adsorption cycle, and another 0.06% loss per additional adsorption cycle, was due mostly to carbon ash. A 1.5% loss of carbon was found when it was treated with 1% NaOH solution. Heating the used carbon in air at 550° C caused the greatest loss of carbon, apparently due to combustion. Thermal activation at 950° C in a CO_2 atmosphere gave 5% loss of carbon.

Disadvantages of Thermal Regeneration

Even though the thermal regeneration technique appears to be more effective in restoring the Cr(VI) adsorptive capacity, the disadvantages of a thermal regeneration system are significant.

Fig. 8—Percent desorption of chromium from the carbon surface by caustic solution.
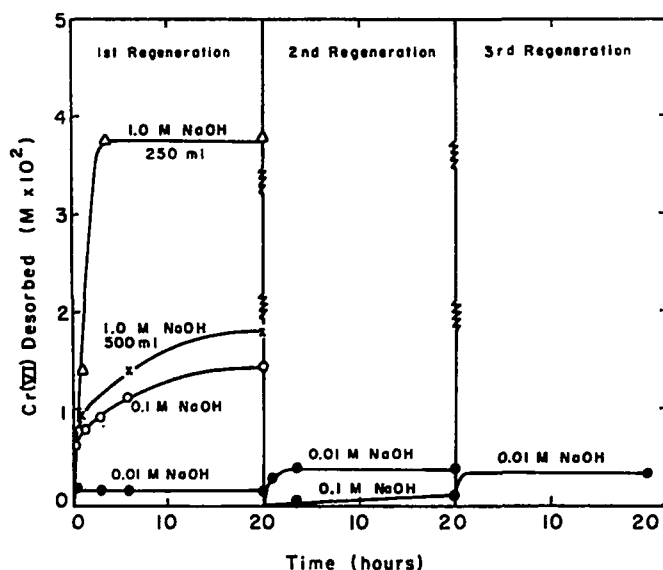

Fig. 9—The concentration of Cr(VI) desorbed in caustic solution as a function of time.

Notice that close to 100% regeneration is achieved by 1.0 M NaOH after 1 cycle for 500 and 250 ml volumes of caustic solution, but the concentration of Cr(VI) is doubled for the solution of lesser volume.

The primary goal of any waste treatment system is to concentrate large volumes of wastewater into a small volume of waste, which is easy to handle and dispose of. Therefore, the purpose of regeneration is not only to remove the adsorbed chromium for the surface, but to concentrate that chromium into the smallest regenerate stream possible. Figure 10 shows the maximum concentration of Cr(VI) that can be collected in the regenerant at various concentrations of caustic solution.

Acidic Desorption of Cr(VI)

Regeneration of the exhausted carbon with strong acid

solution appears attractive in an economical sense, because acid is generally less expensive than caustic. Figure 11 shows the reduction and desorption of adsorbed Cr(VI) from the carbon surface in 0.1 M HCl solution. The desorption in the acid solution is much slower than that observed in the caustic regenerate solutions, however, stronger acid solutions may be used to speed up the reaction and increase the extent of desorption.

In contrast to caustic regeneration, strong acid regeneration can only strip off Cr(III) from the carbon surface. This provides an option for the regeneration of Cr(III)-laden activated carbon.

REMOVAL OF Cr (III)

As indicated previously, Cr(III) production is difficult to prevent in column operations. If the process of packed
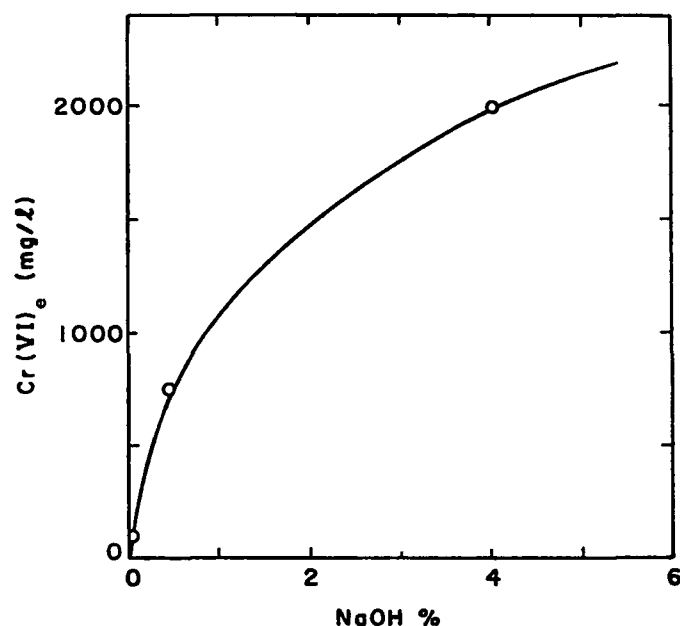

Fig. 10—Maximum Cr(VI) concentration obtainable in regenerant solutions of various caustic strength.
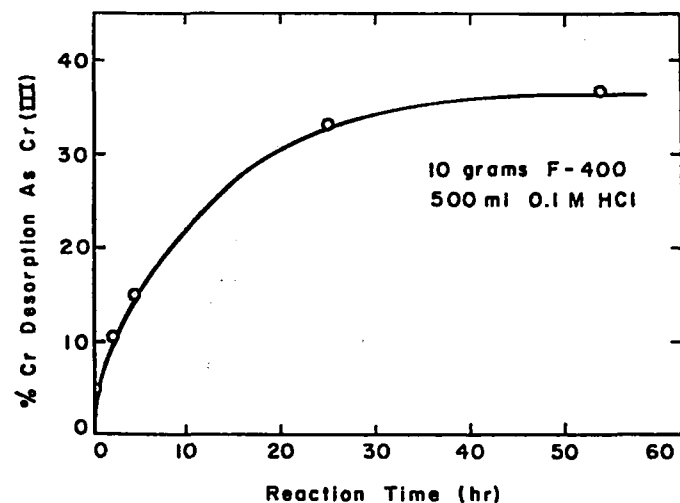

Fig. 11—The desorption of Cr(VI) from the carbon surface in acidic solution as Cr(III).

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carbon column for Cr(VI) removal is selected, the effluent must be treated to remove Cr(III). As indicated by Huang and Ostovic,[7] a different type of carbon is needed for the removal of cations such as Cr(III). Results of the preliminary tests on the adsorption characteristics of Cr(III) by various brands of commercial activated carbon are shown in Table 3.

TABLE 3

Comparative removal by various activated carbons.

Carbon type	pH	% Cr(III) removed/24 hrs
Filtrasorb 100	4	15
Filtrasorb 200	4	9
Filtrasorb 300	4	9
Filtrasorb 400	4	10
Nuchar WVG	4	10
Nuchar WVL	4	17
MCB CX 647	4	14
Darco HD300	4	7

Original Cr(III) concentration = 5×10^{-4} M CrCl₃
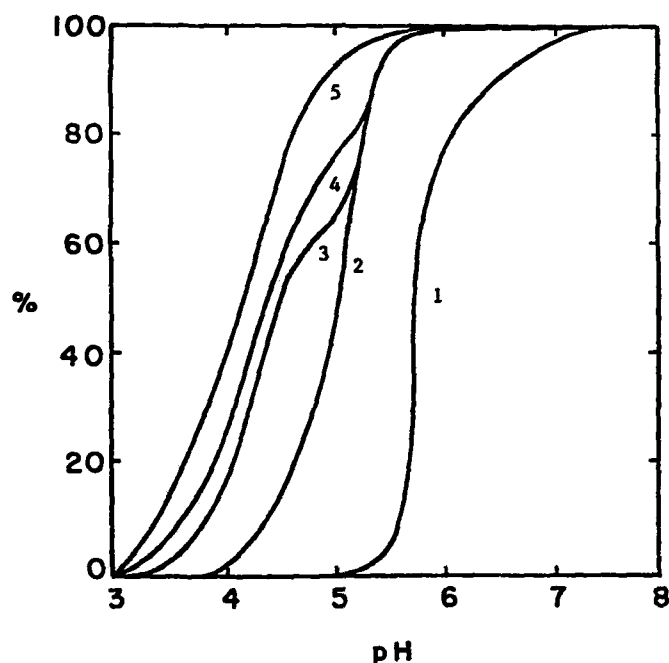Ionic strength = 0.1 M NaCl
Carbon dosage = 29/1

pH

Fig. 12—The percent of Cr(III) by adsorption or precipitation under various conditions.

1. theoretical Cr(OH)₃ precipitation expected without the presence of carbon
2. actual Cr(OH)₃ precipitation observed without the presence of carbon
3. 2 g/l N-VWL
4. 4 g/l N-VWL
5. 6 g/l N-VWL

The percentage of Cr(III) removal appears rather small under this particular set of experimental conditions. However, it is possible to identify the rather promising carbon types: Nuchar WVL, Filtrasorb 100 and MCB CX647.

To improve the percentage of removal, it is important to adjust the pH values to > 4, or to use enough activated carbon (Figure 12). A more thorough investigation on the application of activated carbon for Cr(III) removal is now being undertaken in the authors' laboratory.

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Removal of Heavy Metals
From Battery Manufacturing Wastewaters
By Hydroperm™ Cross-Flow Microfiltration

By Dr. John Santo, Dr. James Duncan & N. Shapira*
Charles H. Darvin**
John Baranski and Kenneth Mihalik***

SECTION I

Regulations promulgated by Federal, State and local governments place strict limits on the quantities of heavy metals which may be released to the environment. In some instances surcharges are imposed. Limits are measured both in concentration and in total mass quantities per day or month. The controlled metals include: Ag, As, Cd, Cr, Cu, Pb, Hg, Ni, Sb and Zn.

This paper describes the results of Phase I of a two-phase program to demonstrate the applicability of the Hydroperm™ microfiltration system for the removal of toxic heavy metals from lead-acid battery manufacturing wastewaters after the metals have been chemically precipitated. This program is being conducted under the sponsorship of the United States Environmental Protection Agency Industrial Environmental Research Laboratory in Cincinnati, Ohio. The results reported herein are from the successful laboratory testing of the system. In Phase II, during 1979, a 24,000 gpd Hydroperm microfiltration system will be constructed and demonstrated at a General Battery Corporation plant.

While the present program is directed toward treating wastes from one specific industry, it is realized that many other industries including the electroplating and metal refining industries also have metal removal problems. It is expected that the Hydroperm system will find wide application throughout these industries.

A number of methods are presently used for metals removal, including chemical precipitation, filtration, electrodeposition, and cementation. However the most widely used process is chemical precipitation. Here, a

chemical agent, usually lime or caustic soda, is added to the wastewater, causing the dissolved heavy metals to precipitate in the form of metal hydroxides. The effectiveness of these chemical precipitation processes is pH-dependent. For a given chemical precipitation process, the efficiency of removal of metals also depends on the employment of a suitable solid-liquid separation system. The types of separation systems in use at present usually involve gravity separation or filtration.

Filtration processes can be divided into two general categories: cross-flow and through-flow filters. In through-flow filtration, the flow of both feed and filtrate are normal to the surface of the filter medium; thus the filtered particles continuously accumulate on and within it (see Figure 1). As a result, the filtrate flux steadily
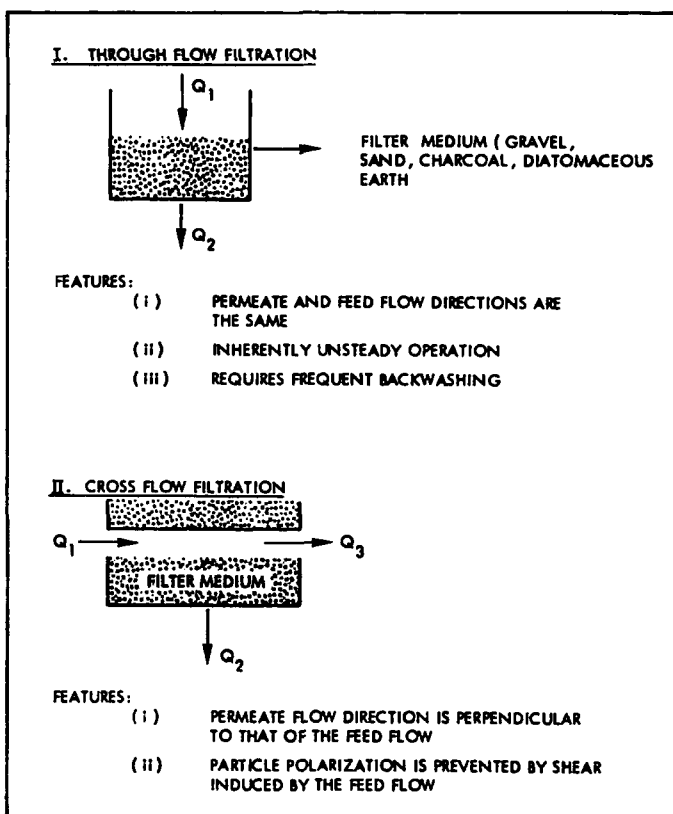

Fig. 1—Types of Physical Microfiltration.

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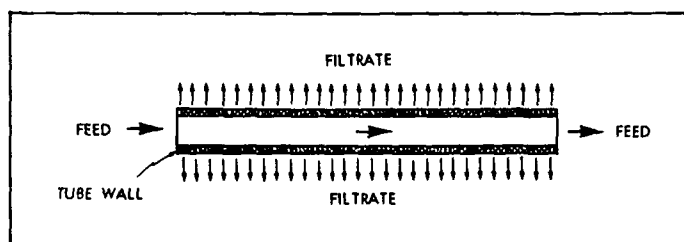General Battery Corporation, Reading, Pennsylvania

Fig. 2—Crossflow Filtration Schematic.

decreases in time when the pressure drop across the filter is maintained constant, and frequent "back-washing" is necessary to remove the accumulated solids from the filter matrix. Multimedia filters and diatomaceous earth filters are two common examples of through-flow filters.

A different type of filtration which has been introduced in recent years is cross-flow filtration, wherein the direction of flow of the wastewater is parallel to the filter surface, with the filtrate permeation occurring in a direction perpendicular to the flow. With this process, a quasi-steady operation is possible, since the continuous build-up of the separated solids on the filter surface is largely prevented by the hydrodynamic shear exerted by the cross-flow (see Figure 2). Examples of cross-flow filtration include microfiltration and membrane filtration such as ultrafiltration and reverse osmosis utilizing tubular filters.

It is relevant to point out that cross-flow **microfiltration** which removes primarily suspended solids, is significantly different from membrane **ultrafiltration** (UF) or **hyperfiltration** (RO) which remove substances on the molecular level in addition to suspended solids. In UF, higher filtration pressures (≥ 50 psi) are used, with even higher pressures (from 600-1200 psi) for RO, compared with only ~5 psi for Hydroperm microfiltration. Furthermore, UF and RO employ relatively **thin** membranes, compared with the in-depth, relatively thick-walled (~1 mm) Hydroperm microfilters. As a result, power requirements as well as both capital and operating costs are much higher for membrane systems than for Hydroperm. Another major disadvantage of membrane filtration systems is that, under the relatively harsh conditions characteristic of industrial filtration applications, they are susceptible to fouling and clogging, leading to unacceptably low filtrate flux levels. Some of the problems associated with membrane systems are listed in Table I below:

TABLE I
DISADVANTAGES OF MEMBRANE SYSTEMS

- Prone to Clogging and Fouling
- "Cleaning" is Complicated
- Require Relatively High Filtration Pressures
- Prone to Leaks
- Relatively High Cost

The Hydroperm microfiltration system which was used for the present tests utilizes thick-walled plastic tubes whose walls are microporous, with the pore structure and sizes being controlled during the manufacturing process. Because of the basic ruggedness as well as the chemical and biological inertness of the tubes, they are not susceptible to the handling, fouling and cleaning problems of membrane systems.

The outline of the present paper is as follows: in Section II the precipitation of dissolved metals, and in particular lead, is briefly discussed since this is the prime importance for the success of any microfiltration system. A description of the principal features of the filter tubes follows in Section III which also contains some qualitative theoretical discussions on filter performance. The experimental apparatus and procedures used in the present study are described in Section IV. Results of tests with battery manufacturing wastewaters are presented in Section V. Section VI describes the complete Hydroperm system planned for the field demonstration. Finally, some concluding remarks are given in Section VII.

SECTION II

The Precipitation of Heavy Metals

The success of the cross-flow, microfiltration process in removing heavy metals will basically depend on the efficiency of the precipitation technique applied **prior** to the Hydroperm filtration. Wastewater from battery manufacturing plants has a low pH which leads to high concentrations of **dissolved** lead. The determination of an optimum pH for the Pb precipitation, even for a single chemical agent, is complex. The presence of other elements, the alkalinity of the water, temperature variation, etc. make it necessary that an optimum precipitation pH is established for each different wastewater.

The solubility of lead in an aqueous solution is substantially affected by pH. Lead dissolves, forming Pb ions in solutions having a pH of 8 or less. In the pH range 8-11, Pb precipitates as lead oxide:

$$Pb^{2+} + 2OH^- \rightleftharpoons PbO + H_2O$$

Because of the amphoteric nature of lead, the PbO dissolves in solution with a pH > 11:

$$PbO + 2H_2O \rightleftharpoons Pb(OH)_3^- + H^+$$

In a Pb-carbonate-water system, the solubility of lead depends on both pH and carbonate ion concentration. In the range of pH 5 - 8.5 Pb precipitates as the carbonate:

$$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3$$
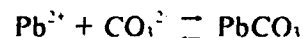
Between pH 8.5 and 12.5 lead is precipitated as either lead oxide or as the basic carbonate:

$$3 Pb^{2+} + 2CO_3^{2-} + 2H_2O \rightleftharpoons Pb_3(CO)_2(OH)_2 + 2H^+$$

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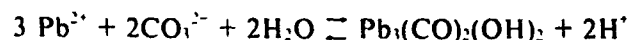
TABLE 2
Feed and Filtrate Analysis

	TS (mg/l)	SS (mg/l)	Pb (mg/l)	Cu (mg/l)	Zn (mg/l)	Ni (mg/l)	Sb (mg/l)	As (mg/l)
Feed	50.312	43,762	8.55	1.74	2.56	1.85	0.57	0.027
Filtrate	2.889	5	0.059	0.027	< 0.027	0.0028	0.35	< 0.002
% Removal	94.26	99.99	99.31	98.45	99.96	99.85	38.6	92.59

Many of the parameters, however, are interrelated. The carbonate-biccarbonate-hydroxide alkalinity ratio is a function of pH. Also, the concentration of calcium and magnesium that may be present in a wastewater is a function of both alkalinity and pH. When several parameters are varied simultaneously, as would be the case during wastewater treatment, it is difficult to predict how Pb solubility will be affected.

Hydrated lime, $Ca(OH)_2$, which has been used in this work, reacts with ionic lead forming lead hydroxide:

$$Pb^{2+} + Ca(OH)_2 \rightarrow Pb(OH)_2 \downarrow + Ca^{2+}$$
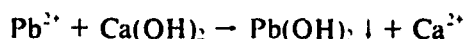
The lime demand of a given wastewater is also a function of the buffer capacity or alkalinity of the wastewater:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2\,CaCO_3 \downarrow + 2\,H_2O$$
$$2\,Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow 2\,CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2\,H_2O$$
$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaOH$$
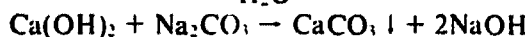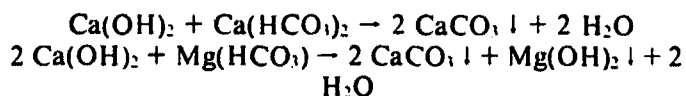
In the case of the General Battery wastewaters, the analytical results (see Table 2) clearly indicate that the optimum pH for the precipitation, and consequently for the removal of the principal heavy metals, falls into the pH range of 9.3 - 9.6.

SECTION III

Characteristic Features of Cross-Flow Filtration

The novel method of suspended heavy metals removal described in the present paper is based on cross-flow filtration with thick-walled, porous plastic tubes. These tubes, which can be made from a variety of extrudable thermoplastics by a proprietary process, have several unique characteristics, including controlled microporosity and ruggedness.

Hydroperm has application in a number of important wastewater treatment roles, as follows:

- **Pretreatment** for suspended solids removal prior to reverse osmosis, carbon adsorption, or ion exchange treatment.
- **Polishing,** for removal of fine suspended solids after chemical or biological treatment.
- **Water Reuse,** when this is otherwise impeded by the presence of suspended solids.
- **In-Plant Processes,** for valuable materials recovery.
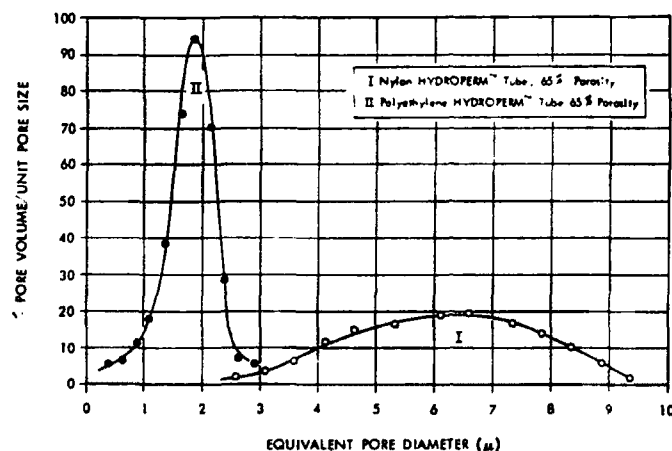- **Toxic Heavy Metals** removal when in fine, suspended form.

Fig. 3—Typical Pore-Size Distributions of Tubes.

- **Treatment for discharge.**

The filtration characteristics of these tubes combine both the "in-depth" filtration aspects of multimedia filters and the "thin-skinned" surface filtration aspects of membrane ultrafilters. For example, while the removal of micron-sized particles and colloids is often impossible with conventional through-flow filters, Hydroperm tubes are capable of removing such particles. On the other hand, in a manner similar to multimedia filters, the tubes will allow the smaller particles and colloids in the waste streams to actually penetrate into their wall matrix. It should be noted that the pore structure of the tubes differs from those of membrane ultrafilters in that the pore sizes of the former are of the order of several microns, with the "length" of the pores being many times their diameters. A schematic view of cross-flow filtration through the tubes is shown in Figure 2. The feed flow is through the inside of the tubes at relatively low pressure (~5 psi) and the filtrate permeation occurs through the relatively thick (~1 mm) tube walls.

Pore-size distributions of two typical tubes are shown in Figure 3. Tube I has a rather "flat" distribution with the pores ranging in size from 3 microns to 9 microns. On the other hand Tube II has a "peaked" distribution, with most of the pores being in the 2-micron range. They can be made from many thermoplastics such as polyethylene, nylon and others.

Two views of the pore structure of a typical tube are shown in Figure 4. These photographs were taken with the aid of a scanning electron microscope and are of a
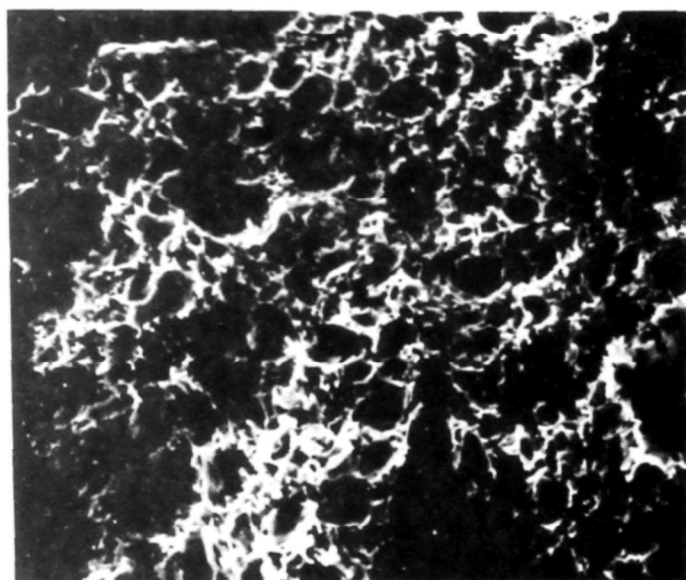
a) S.E.M. 200X
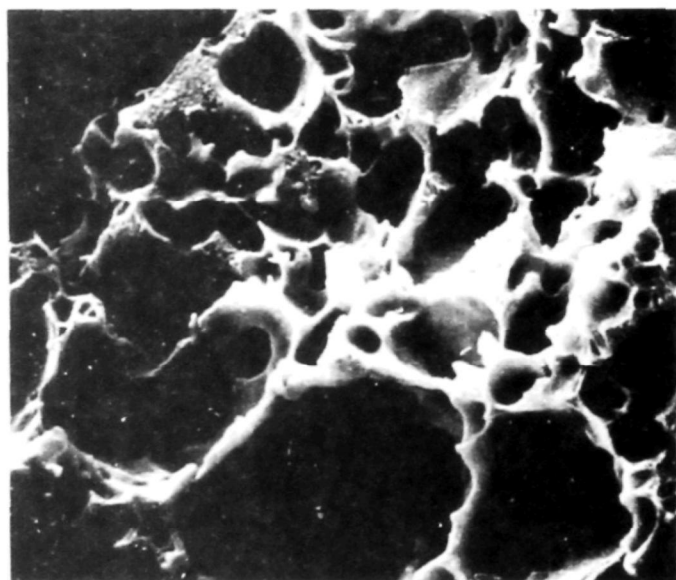
b) S.E.M. 1000X

Fig. 4—Electron Microphotographs of Hydroperm™ Tube Pore Structure - Transverse Section.

transverse section of the tubes; the view in (a) has a magnification factor of two hundred, while that in (b) has a magnification factor of one thousand. The open-cell, reticulated nature of the pore structure can be appreciated from these photographs. These features are of crucial importance in determining the performance of a given tube when it is used with a specific effluent, as can be seen by considering a relatively simple model for the filtration process.

In general, any effluent from which suspended solids removal is desired will contain a wide range of particulates, ranging in diameter from several microns to colloidal dimensions. When such effluents are circulated through the inside of this type of tubular filter, the solid particles will be slowly driven, with the permeating flow, toward the wall. Thus, the concentration of the particles

in regions close to the wall will tend to steadily increase, this tendency being delimited by the turbulent diffusion of the particles from regions of high concentration to those of lower concentration (that is, away from the walls toward the center of the tube).

The turbulent diffusion (which tends to decrease the particle concentration near the wall) is dependent on the shear stress that is exerted on the walls by the cross-flow circulation, and, hence, its velocity. On the other hand, the permeation rate (which tends to increase the particle concentration near the wall) depends on the pressure differential across the filter surface (Poiseuille's law) as well as the pore structure of the tubes (Darcy's law). A quasi-steady state profile of the concentration of the particles will be established near the wall, when the two opposing tendencies mentioned above exactly balance each other. The resulting "particle polarization" in this case is entirely analogous to the "concentration polarization" of solutes that occurs close to walls of ultrafiltration and reverse-osmosis membranes.

Because of the in-depth filtration characteristics of the tubes, other factors also come into play. Specifically, particles which are smaller than the largest pore size of the tubes can actually enter the wall matrix, while particles which are larger than all of the pores in the tubes will be retained at the walls. This feature is illustrated schematically in Figure 5, which shows the particle-size distribution in the feed plotted on the same scale as the pore-size distribution of the filtration tubes. The shaded region represents the particles which are smaller than the largest pore size and can thus enter the wall matrix. These particles will remain within the wall of the tube because of the irregular and tortuous nature of the pores. Thus as filtration proceeds, the pore structure of the tube as well as its permeability will undergo a gradual change due to the penetration of some of the pores by the intruder particles. However, the tendency of new particles to enter the tube matrix will decrease as a fine, dynamic filter cake forms on the walls due to particle polarization described earlier. Clearly, both the change in the pore structure and
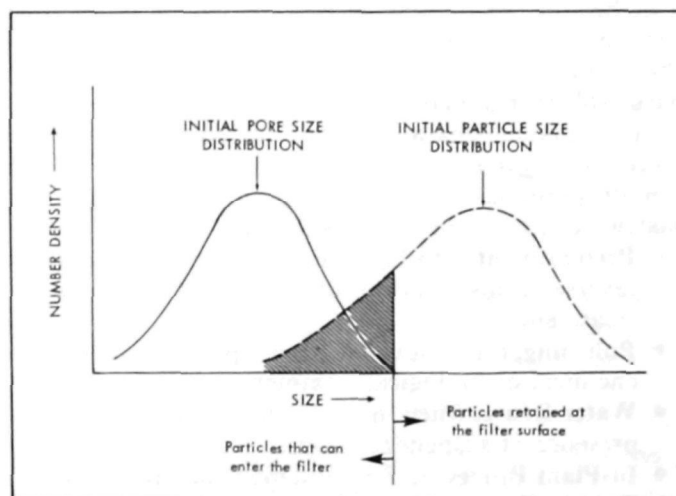

Fig. 5—Schematic of the Suspended Solids Penetration of the Hydroperm™ tube matrix.

the properties of the filter cake will be strongly influenced by the shaded overlap region in Figure 5 and, consequently, so will be the filtration performance.

Even from the relatively simple, qualitative discussion given above, it is clear that the filtration performance is influenced not only by such factors as the filtration pressure, circulating flow velocity and temperature (which changes the fluid viscosity and, hence, by Darcy's law, the permeation rate), but also by the pore-size distribution, pore structure and the particle-size distribution in the wastes. As mentioned earlier, the unique feature of these tubes is that their pore characteristics can be "tailored" (that is, controlled in a systematic manner) to suit the characteristics of a given waste effluent.

SECTION IV

Experimental Apparatus and Test Procedures

The experiments described in the present paper consisted of tests mostly with single tubes, though tests with small modules containing a "bundle" of several tubes are also typically performed. The inside diameters of the single tubes tested were either 4 mm, 6 mm or 9 mm, and they had a length of about 46 cm so that their filtration-surface area ranged from about 57 cm^2 (9 in.^{2}) to 130 cm^2 (20 in.^{2}). A schematic view of a typical single-tube loop is shown in Figure 6. As indicated in the figure, the loops contain a feed reservoir ($\sim$5* gallons capacity), a circulating pump, a flow meter, pressure gauges to measure pressure drops over the length of the tubing being tested and appropriate valving. Portable test loops essentially like that shown in Figure 6, have also been used at plant sites to conduct tests "in situ"

Basically, two different modes of operation are used when carrying out the tests. In the first, which is the one most often used and simulates "continuous-mode-operation in a prototype system, the permeate is remixed into the feed reservoir, so that (except for evaporation losses) the volume of the circulating feed, as well as its suspended-solids concentration, remain constant. The feed in the reservoir is replaced at appropriate intervals to eliminate changes in characteristics due to biological activity and/or constant recirculation.

In the second mode of operation, "concentration", a batch-wise process in a field prototype system is simulated. Here the permeate is collected in a separate reservoir, so that the volume of the circulating feed continuously decreases while its suspended-solids concentration continuously increases. The tests are continued until a specified feed concentration is reached or until the volume of the feed becomes so low that adequate pump suction from the reservoir can no longer be maintained.

Results from a wide variety of tests have demonstrated that the Hydroperm tubes are capable of virtually total

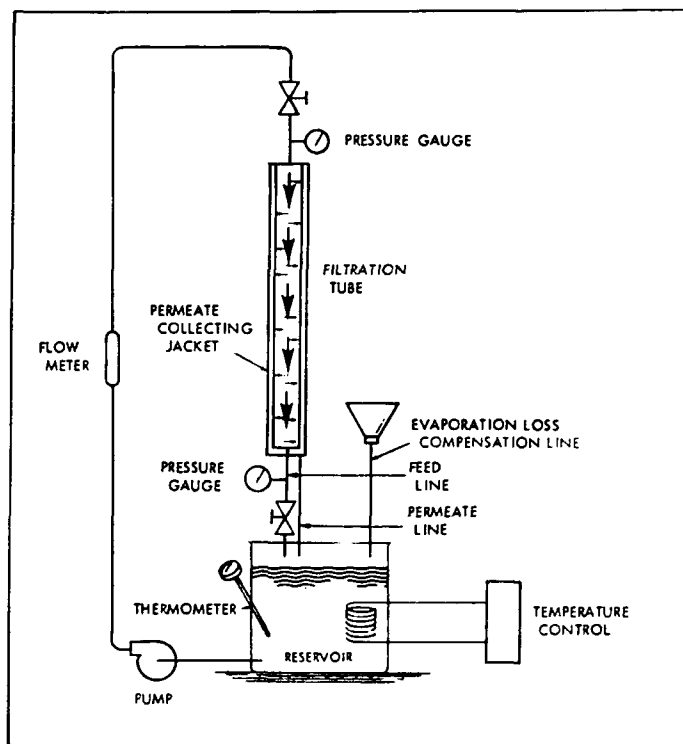* A 55-gal drum reservoir was actually used in this test program.

Fig. 6—Schematic of a Single-Tube Hydroperm™ Test Loop.

removal of suspended (including colloidal) solids at relatively low filtration pressures, and even at high feed concentrations. Indeed, in most cases, the suspended solids concentration in the permeate is nearly independent of the value in the feed, displaying only a negligible residual value. It is also relevant to note that in spite of the micron-size pore structure and the low filtration pressures, in many cases Hydroperm tubes have also yielded significant reduction in dissolved solids. The tubes also achieved complete separation of oil from water.

SECTION V

Tests with Battery Manufacturing Wastewater

The wastewater used for the present tests was obtained from a General Battery Corporation plant. The raw wastewaters contained $\sim$ 1500 - 1900 mg/l of total solids with $\sim$ 20 - 200 mg/l of suspended solids and $\sim$ 10 - 20 mg/l of lead. When received, the wastewater had a pH of $\sim$ 1.2. Toxic heavy metals included Pb, Cu, Zn, Ni, Sb and As. The dissolved metals were precipitated at a range of pH's by adding hydrated lime. The best results were obtained at a pH of 9.3 - 9.6. After lime addition, TS values increased to $\sim$ 45,000 mg/l in the feed, most of which were in the form of SS ($\sim$ 40,000 mg/l).

A number of single tube tests of up to 160 hours in duration were performed with the lime-precipitated waste described above. In all but one of the tests the filtrate was remixed with the feed, which resulted in a "constant concentration" mode of operation. One test was performed with increasing suspended solids

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concentrations in the feed, which resulted from the periodic removal of the filtrate from the feed until an 85% reduction in the total volume of the feed had been reached. The purpose of these tests was to provide information on filtrate flux and quality as a function of the type of tube and the operating conditions used. This information is necessary for tube optimization in pilot-plant design.

A typical plot of filtrate flux versus time in hours is shown in Figure 7. The tube used for this test had an internal diameter of 6 mm and the pore structure was that depicted in Curve 1 of Figure 3. The operating conditions consisted of a feed pressure of 5 psi, a feed velocity of 4 ft/sec and a temperature of 35° C. In this constant-volume test, the filtrate was remixed with the feed. Note from Figure 7 that the flux begins at $\sim$ 1,000 gal/ft^2-day and typically declines almost immediately, with the rate of decline decreasing with time. From this curve and experience with other wastes it can be estimated that steady "plateau" fluxes of from 150 to 250 gfd could be maintained for several days without any tube cleaning. However, after 40 hours in the present test, the tube was cleaned by operating the tube normally with a water solution of 0.25% Servac (a mild phosphoric acid containing commercial cleaner) in water for a period of 15 minutes. Dilute HCl ($\sim$3 %) was also used successfully. Note from the figure that when the test was started again the flux had been restored nearly to its original value ($\sim$1,000 gfd), after which it began to decline again. The second flux decline was not as rapid as it was in the first part of the test. This behavior frequently occurs, probably because of changes in the feed during pumping, and changes in the pore structure resulting from penetration of fine suspended solids into the pore matrix.

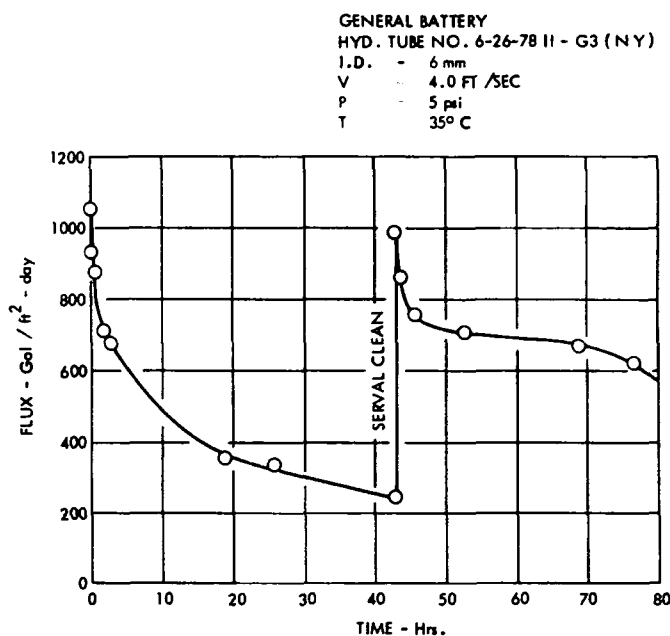A total of twelve single-tube tests have been performed

thus far, with: 2 tube pore types (the ones shown in Figure 3); 3 tube internal diameters (4 mm, 6 mm and 9 mm); with: feed velocities (7 ft/sec and 4 ft/sec); and one feed pressure (5 psi). The results for the constant feed concentration tests in terms of filtrate flux demonstrated the influence of several important parameters. First, the pore structure had a significant influence on flux, since the tube with the wide pore-size distribution had a flux of 250 gal/ft^2-day after 40 hours, while the tube with the narrow distribution had a flux of 50 gal/ft^2-day after only 2 hours of operation. The effect of feed velocity was also significant, since for the 7 ft/sec tests the filtrate flux after 40 hours was about 100 gal/ft^2-day higher than that for the 4 ft/sec tests. The tube diameter, on the other hand, was found to have little or no influence on flux. These findings are consistent with the description of the physics of the filtration process given in Section III. The above results are important for design purposes, since the flux, feed velocity, and tube diameters will all have an influence on economics in terms of materials cost and power requirements.

The flux record for the test which was done with increasing feed concentrations is shown in Figure 8 ($\sim$200 gfd at 160 hours). The tube type is the same as Tube I shown in Figure 3. However, the internal diameter here is 4 mm. The test conditions are given in Figure 8. Note from the figure that the test was operated in the constant-concentration mode for most of the 160 hours of testing, however, during four 3- to 7-hour intervals, the filtrate was removed from the feed. Thus, the concentration of suspended solids in the feed increased in four steps during the test. During the final part of the test, the total feed volume had been reduced to only 15% of its original value. The flux levels in the figure show that, even with this high feed concentration, fluxes of around 200 gallons /ft^2-day can be achieved.

Having established typical flux rates and the dependence of these rates on certain operating parameters, one turns now to filtration performance in terms of filtrate quality. During the above tests, samples of the feed and filtrate were analyzed periodically for total solids (TS), suspended solids (SS), lead (Pb), Copper (Cu), Zinc (Zn), Nickel (Ni), Antimony (Sb), and Arsenic (As). Atomic adsorption was the analytical method used. From these analyses it was found that the filtrate quality was independent of any of the operating

GENERAL BATTERY
HYD. TUBE NO. 6-26-78 II - G3 (NY)
I.D. - 6 mm
V - 4.0 FT /SEC
P - 5 psi
T - 35° C
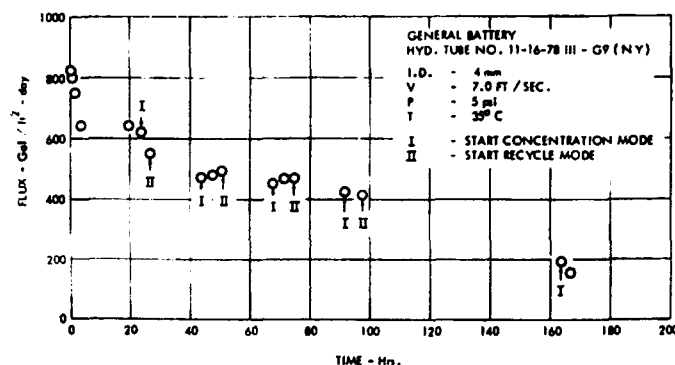
Fig. 7—Permeate Flux Results.
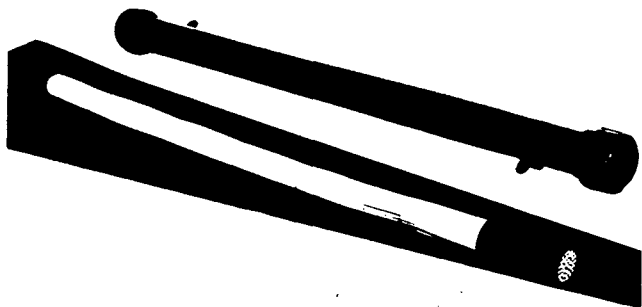

Fig. 8—Permeate Flux Results.

Fig. 9—Hydroperm™ Module.

conditions or tube types mentioned above. A typical comparison of the analysis of the feed and filtrate samples is shown in Table 2. Note from the table that the suspended solids content of the feed of 43,762 mg/l was reduced to 5 mg/l in the filtrate, and that lead was reduced from 8.55 mg/l to .059 mg/l. These excellent rejection percentages also hold for the other heavy metals tested, as shown in the table. However, it should be pointed out that, while microfiltration achieves virtually complete removal of suspended solids, the quantity of total metals converted to SS form is dependent upon definition of an optimum pH for precipitation. In this case, the optimum pH for lead removal is ~9.3 - 9.6.

SECTION VI

The HYDROPERM™ System

The basic element of the Hydroperm microfiltration system is, of course, the tubular filter element that was described in Section III. The design of the **total system** primarily involves combining large numbers of these tubes with a feed reservoir in a manner which is economical in terms of capital and operating costs. The design approach utilized at present is to combine groups of tubes into modules which make up the basic building blocks of any system.

A number of steps are required in total system design, starting with tube optimization and proceeding to component selection and sizing. The modules can be optimized in terms of their length and diameter, number of tubes contained, type of end-fitting used, and so on. A typical module is shown in Figure 9. The arrangement of the modules can also be optimized in terms of whether they are arranged in series, in parallel, or in a combination. The criteria used for the last two optimization steps are ease of handling, ease of maintenance, ease of installation, power requirements, space constraints, as well as capital and operating costs (see Figure 10).

When compared with other systems, the system of this program offers several unique advantages. These are summarized below:

(a) **Compactness:** The microfiltration system does not require large spaces, they can be engineered to fit **available** space.

(b) **Flexibility:** Various estimates place the number of electroplating and metal finishing companies in the U.S. at well in excess of 10,000. Many of these are small. Because of its modular construction, the microfiltration system can be designed to accommodate a full range of wastewater treatment requirements, from small to large.
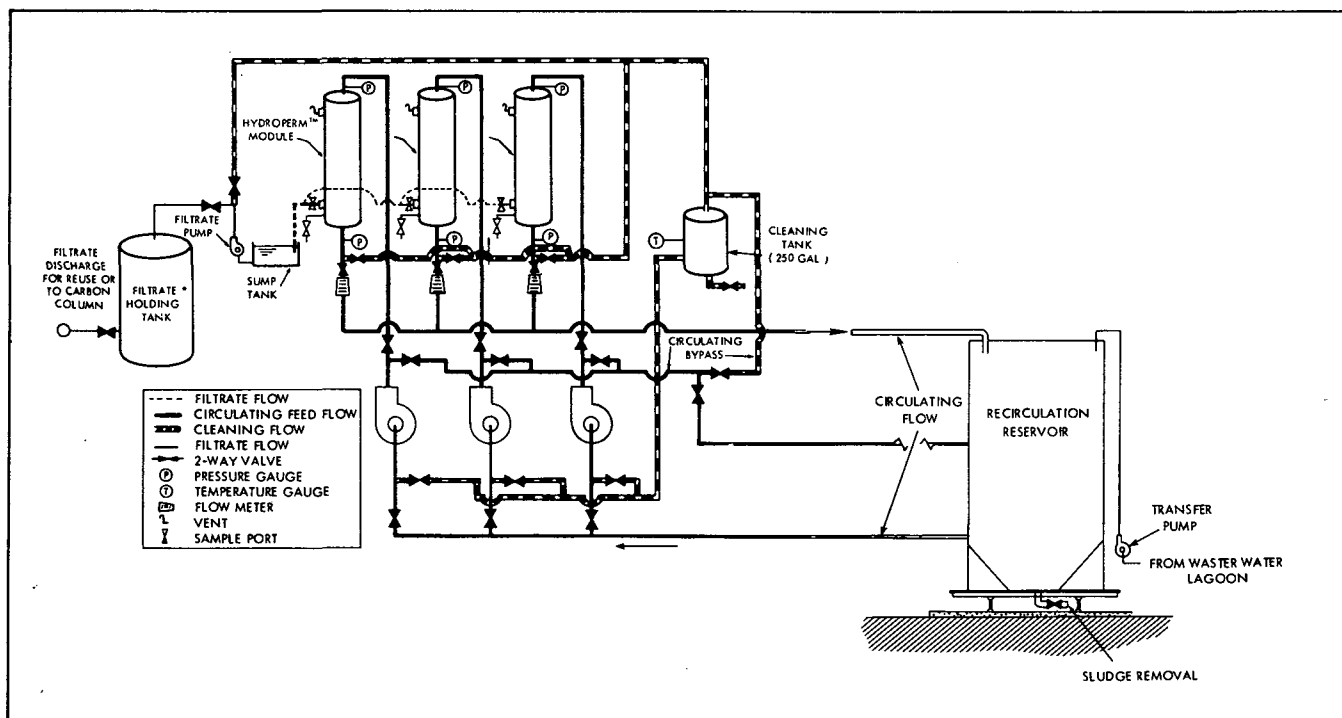

Fig. 10—Schematic Hydroperm™ Wastewater Treatment System.

(c) **Versatility**: Since the microfiltration system is excellent in removal of suspended solids and oils as well as substantial dissolved solids, the permeate can be either directly recycled in cases where the presence of some dissolved solids does not bar such water reuse, or it can be discharged into sewer systems or natural waters.

(d) **Ruggedness**: Since they are made from inert thermo-plastics, the performance of the tubes does not depend, in general, on changes in influent pH. Moreover due to their rugged structure and low operating pressure, the modules are not subject to the fouling and leaking problems which have plagued some membrane systems; nor are they subject to clogging in the presence of oily wastes.

(e) **Ease of Maintenance**: Because of their ruggedness and modular construction, the microfiltration system is easy to maintain. It can be engineered in such a way that a failure in a given module causes only a small part of the total system to be shut down.

(f) **Product Recovery**: In many cases product recovery is possible.

The virtually total absence of suspended solids in the permeate from the tubes makes the permeate ideally suited for ultimate treatment, when necessary, for the further removal of dissolved solids by carbon or resin columns, or RO membranes, so as to produce a completely reusable or dischargeable water.

SECTION VII

Summary

The excellent results of Hydroperm performance in terms of flux and permeate quality reported herein are typical of the use of the Hydroperm separation system with a number of other wastes. It should be pointed out that the results of the heavy metals separation tests described herein are not dependent on either the fact that the wastewater containing the heavy metals is from a battery manufacturing plant or that the metals were precipitated with lime. Removal by Hydroperm of various metals in suspended solid form as a result of precipitation by chemicals other than lime would still be just as effective. Thus, the results described herein would appear to have widespread application throughout the metal finishing industry. If either the waste characteristics or the precipitant were to be changed, it is clear from past Hydroperm tests (with Zn, Cu, Cd and Ni) that results similar to those reported herein in suspended solids removal would be obtained by appropriate changes (if necessary) in tube pore-size distribution and operating conditions. Tube performance in removal of SS is substantially independent of the type of metal or concentration.

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Status of Analytical Methods for Cyanide

Gerald D. McKee*

Introduction

The monitoring of cyanide in waste effluents is required by the U. S. Environmental Protection Agency to determine the "Total Cyanides" and the "Treatable Cyanides," cyanides amenable to chlorination, being discharged to a water body. The EPA approved method[1] for measuring "Total Cyanides" does not measure thiocyanide compounds or organic cyanides that do not decompose or hydrolyze in mineral acid to cyanide ion. The EPA approved method[2] for measuring "Treatable Cyanides" is based on the well known cyanide destruction by oxidation with chlorine or hypochlorite. Total cyanide is measured before and after an alkaline-chlorination treatment of the sample and the difference is termed "Cyanides, Amenable to Chlorination." Several methods have been developed for the determination of cyanides based on the ease of dissociation of cyanide compounds using different experimental conditions. This has brought about a whole host of less than descriptive terms for cyanide, including "free," "simple," "easily dissociable," complex," and "non-dissociable" cyanides. The dissociation of most inorganic cyanide is a function of pH. Heat, catylsts or inhibitory agents are commonly used to increase or decrease this dissociation and subsequent removal of cyanide ion from the sample for measurement. All of the methods discussed use either pyridine-barbituric acid or pyridine-pyrazolone for colorimetric development, titration with silver nitrate or an ion-selective electrode (ISE) for final quantitative measurement of cyanide. These measurement techniques are discussed as a part of the total cyanide procedure.

Methods for Less than Total Cyanide

A method for measuring "free" cyanide using a Conway micro diffusion cell has been proposed for use by the American National Standards Committee on Photographic Processing, PH4.[3] Cyanide measured by this technique is defined in this method as "the cyanide, bound or otherwise, which can easily form hydrogen cyanide (HCN) from an acidified solution." A small sample volume (3 ml) is placed in the outer ring of the cell, treated with cadmium chloride to precipitate hexacyanoferrates and buffered to pH 6. An airtight lid is placed on the cell and the HCN gas diffuses into the center chamber of the cell which contains sodium

hydroxide. This diffusion process takes from four to eight hours to reach equilibrium. Measurement of the cyanide that has diffused into the sodium hydroxide is made with pyridine-barbituric acid. This procedure ;is operator dependent and the cyanides recovered from complex wastes are not well defined.

Mellon Institute developed a method[4] for the American Iron and Steel Institute (AISI) to measure "simple or free cyanides and certain other easily dissociated complex cyanides." Glassware similar to that required for total cyanide measurement is required. The sample is placed in a flask and acidified to pH 4 with sulfuric acid. The HCN formed under these conditions is drawn from the sample by an air flow of 3 litres per minute for 2 hours into a sodium hydroxide scrubber. This method reportedly recovers more than 90 percent of cadmium, zinc, and nickel cyanide complexes and 61 percent of a copper cyanide compound. Ferro and ferri cyanide compounds are not recovered. This method is sensitive to glassware design and rate of air flow.

An electrode technique for measuring cyanide published by Riseman[5] recommended freeing the cyanide ion from metals such as nickel and copper with a preliminary heating step to 50° C for 5 minutes in the presence of ethylene diamine tetraacetate (EDTA). This heating step is carried out on a sample acidified to pH 4 with acetic acid. The sample is then made basic and the cyanide ion measured by a cyanide electrode. This preferential complexing by EDTA releases cyanide ion from some of the metal complexes but cyanide ion present in the original sample is partially lost during the heating step at pH 4.

A similar procedure is published by the American Society for Testing Materials (ASTM), D2306-75, Method C, "Cyanide, Amenable to Chlorination without Distillation (Short Cut Method)."[6] This procedure requires heating the sample to 50°, C for one minute followed by direct colorimetric measurement. The pH of the sample during the heating step is not specified and consequently, very different answers can result from a sample analyzed at different pHs. In addition to the volatility of hydrogen cyanide, if the pH is greater than 12, cyanogen chloride originally present in the sample will be hydrolyzed to cyanate and not measured, thiocyanate if present, will react with the color reagent and be reported as cyanide. This method when used under controlled conditions, such as an individual waste stream with constant characteristics will produce results adequate to aid in required treatment but the lack of

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precisely defined test conditions make this procedure inadequate for monitoring various types of effluent.

The "Roberts and Jackson Method"[7] was developed to measure "cyanide" in the presence of ferrocyanide. The sample is mildly acidified and a heat distillation is carried out under reduced pressure in the presence of zinc acetate to prevent the decomposition and distillation of ferrocyanide. The released cyanide is collected in sodium hydroxide measured with pyridine-pyrazolone.

This procedure has been modified to use an acetate buffer to maintain a sample pH of about 4.5 throughout distillation and is currently being considered for adoption by ASTM. Cyanide is recovered from zinc and nickel complexes but not from ferro, ferri and cobalt cyanide compounds. Recoveries from copper and cadmium cyanide compounds were 72 and 33 percent, respectively.

The Environmental Monitoring and Support Laboratory (EMSL) conducted an interlaboratory study for cyanide analyses, EPA Methods Study 12,[8] that included the Roberts and Jackson, Cyanides Amenable to Chlorination, by Difference and the Total Cyanide methods. Concentrated solutions of potassium cyanide ranging from 13 to 149 ug/l in the presence of iron cyanide ranging from 12 to 223 ug/l when properly diluted were sent to participants. The study participants added these concentrated solutions to a natural water of their choice and analyzed for cyanide by one or all of the methods.

Only three laboratories submitted data for the Roberts and Jackson method and, therefore, the results are of limited value but are presented here because of the method's apparent good precision and accuracy. These data show a 95 percent recovery of potassium cyanide in the presence of iron cyanide and a relative standard deviation of 7.5 percent at a concentration of 80 ug/l.

Cyanides, Amenable to Chlorination[2] is the difference between the measurement of Total Cyanide[1] before and after an alkaline chlorination step. This procedure is the only method approved by the Environmental Protection Agency for effluent compliance monitoring of "Less than Total Cyanide." The chlorination step is carried out at a pH between 11 and 12 for one hour while maintaining an excess of chlorine.

EMSL has used this method to less than 50 ug/l cyanides amenable to chlorination and estimate the intralaboratory relative standard deviation to be approximately 30 percent at 80 ug/l. At this same concentration, in EPA Methods Study 12, this procedure was found to have a positive bias of 141% using pyridine pyrazolone, 106% using pyridine barbituric acid, and 120% using the ISE for the final measurement system. The interlaboratory relative standard deviation was determined to 69, 73, and 126 percent using pyridine-pyrazolone, pyridine barbituric acid and the ISE, respectively at 80 ug/l of cyanide amenable to chlorination.

Methods for Total Cyanide

An automated method using a continuous flow thin film evaporation for dissociable cyanides and high intensity ultraviolet irradiation to decompose ferri, ferro and cobalt complexes (total cyanide) was developed by Kelada.[9] This method also includes a measurement of oxidizable (using ozone) cyanides and thiocyanates by difference. This method is rapid and precise, but some difficulties have been experienced with various degrees of cyanide complex destruction using different UV light sources. Technicon has a method similar to the method of Kelada.

The EPA approved procedure for Total Cyanide[1] is an acid refux distillation. The sample is made highly acidic and magnesium chloride catalyst is used to aid recovery of iron cyanide compounds. The cyanide released from the sample is absorbed in a sodium hydroxide scrubber solution and the cyanide is measured either colorimetrically or titrimetrically. The ISE measurement technique is currently being investigated but is not currently an approved technique for National Pollutant Discharge Elimination System (NPDES) monitoring.

In the EPA Methods Study 12 to determine the precision and accuracy of the total cyanide procedure, data were calculated separately for those analysts using the pyridine-barbituric acid, pyridine-pyrazolone and the ISE. For concentrates added to natural water of the analysts choice, the interlaboratory relative standard deviations at 240 ug/l total cyanide were 18 percent using pyridine-pyrazolone, 30 percent using pyridine barbituric acid and 38 percent using the ISE. The percent recovery using pyridine-pyrazolone was 96 percent, 91 percent using pyridine barbituric acid and 100 percent using an ISE.

Although this study did not include a concentration quite as high as 640 ug/l, calculated estimates of relative standard deviation based on this study are consistent with intralaboratory data and are presented with that qualification. The interlaboratory relative standard deviation at 640 ug/l total cyanide are estimated to be 13 percent using pyridine pyrazolone, 27 percent using pyridine-barbituric acid and 28 percent using the ISE.

Intralaboratory studies estimate the relative standard deviation from 240 to 640 ug/l total cyanide to be between 11 to 14 percent with a detection limit of about 20 ug/l total cyanide.

Problems Associated with Total Cyanide Methodology

As you are aware, the proposed rules for total cyanide discharge limit are: 240 ug/l for a 30-day average and/or 640 ug/l for a daily maximum. I will confine my discusion to analyses of total cyanide at these concentration levels.

As with any analyses, the number of manipulations involved increases the potential for error in the final result due to the variability introduced at each step.

The first step that error may be introduced is immediately after sample collection. The alkaline-chlorination decomposition of cyanide is well known and, therefore, chlorine, if present, must be removed

prior to preserving the sample with sodium hydroxide. The procedure states that the sample should be checked with potassium iodide-starch test paper (KI-starch paper) for the persence of oxidizing reagents. There are a number of reports about the insensitivity of the KI-starch paper. It was reported by one individual (EPA-Region I) that the KI-starch paper being used did not detect less than 10 mg/l chlorine; other users have verbally reported detection limits of 5, 2, 0.5 mg/l chlorine. The KI-starch paper must be kept dry and out of sunlight if the sensitivity is to be maintained. Certainly, there will be significant differences in reported concentrations of cyanide if these high levels of chlorine are present in some samples when the sample is preserved with sodium hydroxide to a pH of 12.

Two other optional pretreatment steps may affect the final results. Sulfides, if present in the original sample, will also distill under the acid conditions as hydrogen sulfide and be trapped in the alkaline scrubber resulting in an adverse affect both in the colorimetric and the ISE procedures. The approved method recommends a test for the presence of sulfide using lead acetate test paper. If present, the sulfide is removed from the sample by filtration following precipitation with cadmium carbonate. Both the initial test for sulfide and its subsequent removal have a potential for producing error. The first error is the possibly poor sensitivity of the lead acetate test paper to detect low levels of sulfide and the second is the treatment with cadmium carbonate and filtration step. Formation of the precipitate and filtration may sorb some of the cyanide complexes and whether this process is physical, mechanical or a loose chemical attraction, the porosity of the filter paper, rate of filtration, time required for the cadmium sulfide precipitate to form, pH, solids originally present in the sample, and the amount of precipitate formed will affect the amount of the cyanide present in the filtered sample.

Fatty acid removal is another step that may introduce error but is not pertinent to this industrial waste.

Another area of potential imprecision in the determination is the rate of distillation. This is a minor area of concern and lessens as the analyst acquires experience with the procedure. The rate of the vacuum distillation changes and requires readjustment as heat is applied to the sample in order to maintain a contact rate of distillation.

Another area of the analysis that may cause differences in the reported concentrations is the use of different catalysts in the distillation step. The procedure as written in the 1974 edition of Methods for the Chemical Analysis of Water and Wastes states that copper chloride is to be used as the catalyst. The December 1, 1976 Federal Register, Vol. 41, No. 232[10] references the 1974 EPA method but a footnote in the Federal Register recommends the use of magnesium chloride ($MgCl_2$) for samples suspected of having thiocyanate present. Other referenced procedures in the above cited Federal Register recommend the optional use of these catalysts. The use of

different catalysts in some sample types will result in widely differing reported concentrations and the catalyst used must be known when comparing data. The 1979 Methods for Chemical Analysis of Water and Wastes will include only the use of $MgCl_2$.

The procedure used for preparing a standard curve can also produce an inherent and unnecessary wobble. If the standard curve is prepared using non-distilled standards, the curve will be approximately ten percent more precise and also more accurate than distilling all of the standards since any error introduced during distillation is eliminated. It is essential that the identical concentration of sodium hydroxide be used to prepare the standards as will result from dilution of the scrubber solution.

Then after preparing a standard curve using non-distilled standards, the distillation technique should be checked by distilling standards. This procedure for standard curve preparation is also less time consuming and will produce a more precise and accurate standard curve and also ensure the entire procedure is working well.

There are two approved procedures for measuring the cyanide in the sodium hydroxide solution of concentration levels of interest. Either pyridine-barbituric acid or pyridine-pyrazolone may be used to develop a cyanide complex that may be measured colorimetrically. The time of reaction for the cyanide and the chlormine-T and the time of reaction between the cyanogen chloride and either color reagent must be kept identical with the standards and samples. This is especially critical for pyridine-barbituric acid. The 1974 approved procedure recommends adding the color reagent immediately after addition of the Chloramine-T; better precision is obtained when this time for reaction between cyanide and the Chloramine-T is held constant at about two minutes prior to addition of the color reagent. Many of these problems have been corrected in the 1979 edition of Methods for Chemical Analysis of Water and Wastes.

Summary

The Roberts and Jackson method for "less than total cyanide" is not an EPA approved Method but based on limited data appears to be adequate for measuring cyanides except for cobalt and iron cyanide complexes and is accurate and precise.

The EPA approved method for measuring "less than total cyanide," Cyanide Amenable to Chlorination, involves two complete measurements for total cyanide and a chlorination step. This procedure has an interlaboratory relative standard deviation approximately 70 percent at the proposed limit for Cyanides Amenable to Chlorination.

The approved procedure for Total Cyanides is a classic procedure that requires analyst experience. The procedure is accurate and has an interlaboratory relative standard deviation of 13 to 18 percent using pyridine pyrazolone for color development at the proposed discharge limits for Total Cyanide from the Electroplating Point Source Category.

All analytical methods, even when used in the best laboratories by the best analytical chemists, require an adequately implemented quality assurance program that includes proper calibration, routine calibration check, analyses of duplicate and spiked samples and laboratory participation in round-robin studies.

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Prudent Waste Treatment Monitoring, Analytical Control, and Testing

By Frank Altmayer*

ABSTRACT

It is not difficult to find reports of fish kills, chemical spills, and discharges of insufficiently treated waste in your daily newspaper. The tragic element in these stories is that a majority of these catastrophies could have been avoided if adequate monitoring and control of waste treatment systems had been performed. This paper shall detail the simple analytical and monitoring tools available for achieving good waste treatment.

All of you work for companies which have recently added a new product line. This new product differs from your ordinary lines of business in many ways, and yet there are some important similarities. This new product must meet constantly increasing quality requirements; its consumer products safety liability aspects are at least as frightening as for any other products you manufacture. The cost of raw materials to produce it are increasing rapidly and yet your customer is a reluctant recipient who charges you for accepting it, and this product, therefore, creates negative sales. Your new product is ecologically acceptable waste water.

As with any other product, the production of a satisfactory waste water requires not only a manufacturing facility commonly called a waste treatment system but careful step by step control of the entire process of waste treatment. One should consider waste treatment a manufacturing process and apply the same monitoring as are common in production of other manufactured goods. These would include controls to insure a consistent treatable raw material, process control, in process inspection, and final inspection. The purpose of this paper is to discuss the simple tools that are available for achieving effective monitoring.

CHOOSING THE CONTROL TECHNIQUE

When choosing the control method for any phase of waste treatment a prudent evaluation must be made as to the degree of control necessary. For instance, for the first step of chlorination of a cyanide effluent it is necessary that the pH remain above 10.5; but a pH of 12 or higher will create no problems. On the other hand, for optimum clarification of mixed metal effluents, it may be necessary

to control the pH to ± 0.1 units. The control methods will vary greatly for these two operations.

Another way in which the necessary degree of control and preciseness of measurement would vary would be whether one's effluent closely approaches the legal limits or if it meets it very comfortably. A company that discharges zinc to a Metropolitan Sanitary District with a limit of 15 mg/l will require a different degree of monitoring if their effluent is consistently in the 5 to 7 mg/l range than if its discharge is consistently 12 to 14 mg/l. In the latter case, they either should improve their waste treatment to have a greater margin of safety or have a very precise control of each phase of treatment.

The selection of control method should also be based upon availability of materials and equipment and operating materials, operator skill required, time for testing, accuracy and precision obtainable, and acceptance of test results by others, if required.

Chemists and waste treatment operators tend to be empire builders. They frequently fall in love with precise, expensive equipment. This characteristic, if unchecked, often leads to poor waste control. For instance, hourly observance of the pH using pH papers accurate to ± 0.2 pH units is more effective monitoring than once a day monitoring using a pH meter accurate to ± 0.01 pH units.

A wide variety of "tools" are available in waste treatment. They vary from the very simplest to very sophisticated. The goal should be to use the simplest, effective tool. Some of these are:

A Waste Treatment Manual

It is surprising how few companies have a manual describing the waste treatment equipment, the function of each separate section, and the proper control monitoring. Such a manual is a must for effective waste treatment. In addition to the above, the manual should detail the type and frequency of inspection to be carried

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out at each treatment step and the remedial steps to be taken in case of an upset.

Sight and Smell

The most important aspect of monitoring a waste treatment system involves the use of one's sight and sense of smell, and yet, very few waste treatment manuals adequately instruct the operators on what to observe, the frequency of observation, or the significance of what they are observing.

A big fear, for any company discharging waste waters, is the catastrophic failures that cause fish kills, sewer dissolution, or other tragic occurrences. These are almost always caused by gross malfunctions detectable by smell or sight. Waste treatment control requires properly trained operators to keep their eye and nose on the entire operation. An operator who notices a yellow color in a chromium reduction tank knows that he is not achieving satisfactory chrome reduction regardless of what his instrumentation shows. A strong smell of chlorine during cyanide destruction indicates gross overchlorination or chlorination at too low a pH. A nearly clear discharge to the clarifier would indicate improper pH adjustment. Too high a sludge blanket or floaters in a clarifier are a sure sign of trouble. Incoming water for treatment exhibiting an unusual color or turbidity will warn an alert operator of potential danger.

pH Papers

Narrow range pH papers are a must for waste treatment monitoring. They enable one to determine the pH at any stage of waste treatment in less than 20 seconds using less than $10.00 worth of equipment, nothing breakable, they are portable, and there is no clean up after the test. They are extremely useful in process control and in checking pH control meters.

Starch Iodide Papers

Potassium Iodide/Starch indicator papers are invaluable aids in monitoring alkaline chlorination of cyanide effluents. They are the only control necessary for batch chlorination and are useful for monitoring the performance of ORP controls on flow through systems.

Test Kits

Two companies have made outstanding contributions to waste treatment control by developing test kits for analyzing waste waters and process waters. They are: Hach Chemical Company; Ames, Iowa 50010 and LaMotte Chemical Company; Chestertown, Maryland 21620. Both of these companies sell a variety of testing equipment ranging from simple color comparative tests costing about $20.00 for each parameter to be measured, to elaborate spectrophotometric kits costing $500.00 to $1,000.00. Generally speaking, we found these test kits useful for process control and rough monitoring when co-ordinated to a specific waste. The cheapest, most simple ones are the most useful and that when it comes to the elaborate ones one would be better off buying conventional non-packaged equipment.

Test kits are extremely useful for waste treatment control-

(a) when used as recommended by the supplier,

(b) when used as recommended by the supplier but corrected to an approximate value using a correction factor determined experimentally, and

(c) when used as recommended by the supplier on samples which have been given more extensive preparation than recommended by the supplier.

Test kits are formulated to compensate for interferences experienced in a wide variety of wastes. For many plating and printed circuit wastes, test kits will give precise results when used as recommended by the supplier. This can be checked out by performing a few analyses on your waste and comparing the results to those obtained using more precise methods.

If a wide discrepancy between test kit results and precise analytical measurements is found, all is not lost. In most instances where the test kits were not precise, the results were repeatable and were off by a uniform predictable value. If this is true for your effluent, a test kit can be used by applying a correction factor for your specific effluent. For example, a company we worked with was having considerable trouble controlling cyanide. Part of the problem was that a precise cyanide analysis required 1 ½ to 4 hours and the services of a skilled laboratory technician. By using a Hach test for cyanide they were able to make a cyanide determination in 20 minutes, using plating department personnel. They found that for their effluent a Hach reading of 1.3 mg/l cyanide corresponded to 2.0 cyanide amenable to chlorination and a Hach reading of 4.5 mg/l cyanide corresponded to 10 mg/l total cyanide.

An alternate to a correction factor can be to pre-treat the sample to eliminate the interferring material. Especially for metal analyses, acidifying the sample with nitric acid and digesting for ½ to 2 hours may destroy the interferring element and enable one to use the test kit satisfactorily.

The suppliers of the test kits will often help you on this.

Just as a warning, don't expect to win a court case based on test kit data if the opposition has used "Standard Methods." In case of a fish kill or citation by a regulatory authority, the test kit results will not stand up unless you have well documented correlation between such results and results obtained using "Standard Methods." Even then, the only value the test kit results will have is to show good faith on your part, rather than to prove compliance.

Specific Ion Electrode

The specific ion electrodes have almost no value as tools for monitoring waste treatment systems. Discharge regulations relate to total pollutant and this varies widely from ion concentration. Ion concentration depends on temperature, pH, other materials present.

Acceptable Analytical Techniques

Three "bibles" are available which describe the best, most precise, universally accepted methods of analyzing waste waters. They are: "Standard Methods for the Examination of Water and Wastewater," published by American Public Health Association; "Annual Book of ASTM Standards," Water, Part 31; and "Methods of Chemical Analysis for Water and Wastes," the Environmental Protection Agency. Most of the procedures in these three books are either identical or very similar. Early regulations specified that the tests were to be to "Standard Methods." The U. S. EPA now reference their method of analysis, and the ASTM Standards perhaps have the highest industrial acceptance. An analysis conducted to the procedures in any of these three books will be admissable as court evidence. However, as a political decision, it is smart to determine, when possible, what method is being used by the regulatory authority you report to and then using the same method.

In order to understand principles of analysis and to develop the skills within your laboratory, I think it is wise to study the procedures for a specific analysis in all three books. ASTM goes into greater detail in describing potential interferences and how to off-set them. Generally speaking, ASTM also gives a greater number of test options. "Standard Methods" is similar to ASTM in their advising how to avoid pitfalls. Such information is useful not only in developing skills and conducting the analyses but are useful if you are trying to adapt Hach or LaMotte test kits to your specific situation. The U. S. EPA methods of analyses tend to be more dogmatic, but it is simpler for most technicians to follow. U. S. EPA has a companion manual entitled, "Analytical Quality Control." This book is most useful for keeping an analytical laboratory from wandering and becoming imprecise.

The U. S. EPA furnishes a very useful tool to waste water control labs to aid in their quality control. The Environmental Monitoring and Support Lab., Environmental Research Center, Cincinnati, Ohio 45268, will furnish vials of prepared solutions containing precise amounts of contaminants and a code sheet stating the amount of these contaminants. The person in charge of lab quality control can give these vials to the chemists or technicians for analysis and when the results are obtained they can be compared to the correct answer furnished by the EPA. These cross checks go a long way towards keeping everyone on their toes.

Periodic Impartial Sampling, Analysis

The effect of citations (fines, bad feelings) can be minimized by having periodic sampling and analyses performed by an impartial outside laboratory. A hearing officer will be inclined to be lenient if a company can show consistent compliance prior to and after a violation.

This system also keeps the waste treatment system operator on his toes.

To sum it all up, for control the most easily conducted test that will suffice should be used. These tests should be done very frequently, perhaps 3 to 4 times a shift, certainly, at least once a day. To verify conformance to regulations, to establish the validity of sample tests, and for all data to be published in the literature, the testing should be done in conformance with "Standard Methods," "ASTM Standards," or, the "U. S. EPA Methods" by an independent laboratory exercising rigid quality control.

Evaluation of Solvent Degreaser Emissions

Vishnu S. Katari, P.E., Richard W. Gerstle, P.E. and Charles H. Darvin

INTRODUCTION

Volatile organic compounds (VOC) are emitted from a number of man made and natural sources. Typical among the natural sources are volatile tupentine from trees which are common in a number of wilderness areas such as the Blue Ridge Mountains of Virginia. Nature in her own way can accommodate and assimilate these VOC emissions. On the other hand, man made VOC emissions frequently represent a quantity which nature may have trouble tolerating. One result of VOC emissions is demonstrated graphically in the form of smog typical to many of our larger cities. It has been estimated that the total nationwide emissions of man made VOC is approximately 28 million metric tons (31 million tons) per year. Of this quantity, approximately 950,000 metric tons (1,045,000 tons) per year comes from some form of solvent degreasing operations.

Solvent metal cleaning can be divided into three main categories: cold cleaning, conveyorized vapor degreasing and open top vapor degreasing. This research and development program evaluates practical and relatively simple methods of significantly reducing organic solvent emissions rates from open top vapor degreasing systems. Even though this research evaluation program is still in process, this paper has been prepared and presented to indicate interim results. A final report will be prepared and published at the completion of this study; it will address the results of this study in detail.

BACKGROUND

There have been for a number of years solvent emission control techniques that can recover or eliminate solvent emissions from degreasing units. They include the use of carbon adsorption or incineration. Carbon adsorption is the process of removing molecules from an emission stream by contacting them with activated carbon. Incineration is the process of thermal destruction of organic molecules. The feasibility of these processes depends on plant economics and fuel availability.

Due to the potential economic impact that the use of incineration or carbon adsorption may impart, particularly on small job shop operations, this research program was initiated by the Metals and Inorganic Chemicals Branch of the Industrial Environmental Research Laboratory. The program was designed to evaluate the capability of less expensive, although, possibly less efficient concepts of control of VOC emissions from vapor degreasers. Therefore, it is believed that the Metals and Inorganic Chemicals Branch through this research and evaluation program can make a significant contribution to both industry and the goals of EPA in identifying cost-effective and efficient VOC control techniques for solvent degreasers.

A number of EPA and industry studies have identified possible options for this purpose. Limited experimentation has indicated that the use of such options as increased freeboard heights, automatically sealed tops, and/or secondary condensers could significantly reduce the rate of organic emissions from degreasers. A secondary advantage of these options would be that they would not require major changes in plant operation or equipment. Thus, they could provide an inexpensive, simple-to-operate method of reducing solvent emissions from degreasers.

Although previous studies have indicated solvent savings, to date, no detailed quantification of the savings potential of these concepts has been documented. Therefore, to determine definitively the capability of these techniques, a controlled test program was initiated. The ASTM committee D-26 on degreasing was requested to assist the testing contractor, PEDCo Environmental, Inc., of Cincinnati, and EPA in defining and formulating this test program. A special sub-committee of D-26 was established for this purpose. Over 25 manufacturers of degreasing systems, solvents, and users were contacted for advice and support of the program. In addition, representatives from NIOSH and OSHA were contacted. Thus, influential groups that are involved in solvent degreasing regulation, specification and utilization were contacted for their comments and assistance.

TEST PROGRAM

A review of the typical vapor degreasers and their design features, and recommendations from previous studies led to selection of the following significant variables for evaluation in this test series:

1) Cover utilization
2) Freeboard height
3) Refrigerated chiller (secondary condenser)
4) Lip exhaust
5) Hoist system speed
6) Load cross-sectional area
7) Solvent type

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Cover

Tank covers are an integral part of most vapor degreasers and are used to cover the vapor zone when idling or shut down. Many covers are left open and not used. The amount of solvent that can be saved by utilizing covers will be measured in this program.

Freeboard Height

Freeboard height is the distance from the top of the vapor zone to the top of the degreaser tank. The primary purpose of the freeboard is to reduce air movement near the interface between air and solvent vapor. The Occupational Safety and Health Administration (OSHA) currently requires a freeboard-height-to-degreaser width ratio of at least 0.50 or 91 cm (36 inches), freeboard height whichever is shorter, for all vapor degreasing tanks with a condenser or vapor level thermostat. OSHA also requires a ratio of 0.75 when the solvent is methylene chloride or trichlorofluoroethane. Past studies reported a 27 percent reduction in solvent emissions in an area of undisturbed air by increasing the freeboard-to-width ratio from 0.50 to 0.75. A 55 percent emission reduction was measured in turbulent air area by increasing the ratio to 1.0.[2]

Refrigerated Chiller (Secondary Condenser)

All vapor degreasers have a primary condenser which utilizes cooling water to control the vapor height. Two types of chillers are currently used above the primary condenser for additional or secondary cooling; one operates at sub-zero temperature of -23 to -32° C (-10 to -25° F) range and the other operates at 1 to 4° C (34 - 40° F) range. The primary purpose of these chillers is to reduce the rate of solvent loss from the top of the degreaser.

Previous tests on a open vapor degreaser with the subzero chiller using methylene chloride showed 40 to 43 percent solvent emission reduction.[2]

Exhaust

A lip vent exhaust can control the ambient air vapor concentration around a degreaser by pulling the air and vapor from the top of the degreaser. However, this may increase solvent consumption unless a solvent recovery system is used. One of the test degreasers will be used to collect data on solvent emissions at exhaust rates of approximately 15.2 to 30.5 m/min (50 and 100 ft/min) face velocity.

Hoist System Speed

In degreaser operation a load is lowered and removed by a vertical hoist system. The vertical movement of the load into the degreaser generates a pumping or piston action and increases emission rates by displacing the vapor blanket. The current recommended maximum hoist speed is 3.35 m/min (11 ft/min.). The testing is conducted at hoist speeds of 2.44 m/min (8 ft/min) and 4.88 m/min (16 ft/min) to determine the difference in solvent consumption.

Load Cross-Sectional Area

The ratio of the load cross-sectional area to the degreaser opening area is an important operating factor affecting solvent consumption because of the pumping action produced by the load movement. The recommended maximum ratio of areas is 0.50 when using many typical solvents. Solvent consumption is being compared at load to degreaser top open area ratios of 0.50 and 0.70.

Solvent

Many different solvents are used in industrial vapor degreasers. Because solvent characteristics such as density, boiling point, and vapor pressure can interact with other variables to generate unpredictable emissions, this program will test at least two common solvents under various operating conditions.

Methylene chloride and 1,1,1-trichloroethane are being used in this test series. Grease deposits that melt only at high temperatures may require a solvent with a high boiling point such as trichlorothane [68° C (165° F) boiling point]. To clean metals sensitive to temperature, methylene chloride [40° C (104° F) boiling point] or trichlorotrifluoroethane [47° C (117° F) boiling point] would be a likely choice. Energy considerations also favor solvents with a low boiling point.

DEGREASER SYSTEMS AND TEST FACILITY

In the beginning of the program, three options were available for testing:

1) Equip a mobile testing facility for on-site testing of degreasers during operation,

2) Use equipment now set up for testing at various degreaser manufacturing facilities, or

3) Borrow degreasing equipment from manufacturers and ship them to PEDCo's test laboratory.

After carefully considering these options, it was decided to design a test facility and borrow the degreasers from manufacturers. This option enhances the ability to accurately monitor solvent emissions, and to better control the test variables and operating conditions.

Several major manufacturers of vapor degreasers were contacted in regard to design features of their systems and some degreaser systems were examined at the manufacturer's facilities. Basic designs do not vary greatly. Only a few manufacturers make degreasers of all sizes and types, and can supply most of the market requirements. The others limit their production either to a particular type (e.g., ultrasonic systems) or a particular size [e.g., small 0.6 by 0.6 m (2-by 2-ft) units]. All provide a cover, a definite freeboard height, and a system of primary condenser coils. Typically, the degreaser unit is also equipped with secondary condenser coils (refrigeration chiller).

Three degreasers were selected: Degreaser A is equipped with an above-freezing temperature secondary condenser system and can be modified for variable freeboard heights. Degreaser B is equipped with a below-freezing temperature secondary condenser system and can be modified for variable freeboard heights.

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Degreaser C is a small unit sized for a freeboard-to-width ratio of 75 percent. Degreasers A and B are of typical size [1.5 m long, 76 to 91 cm wide, and 76 to 91 cm freeboard height (60 in. long, 30 to 36 in. wide, and 30 to 36 in. freeboard height)], with vapor space dimensions which are most frequently used for industrial vapor degreasing, especially in small job shops and metal-working shops.

The test facility is designed with heating and air-conditioning systems to maintain constant ambient conditions of temperature and humidity. Currently degreasers A and B are located in place side by side. Necessary utility connections are in place and tests are being conducted.

DEGREASER TEST PLAN

Table 1 presents the test plan designed to develop quantitative relations between different design variables and solvent losses. The test plan consists of two phases. During Phase I the effects of selected variables on solvent consumption and the interaction between variables will be determined using 1,1,1-trichloroethane. During Phase II, most of the Phase I experiments will be repeated while using methylene chloride. These two solvents are selected because the properties of each are extremely different.

The results of tests will be analyzed to establish the relationships between freeboard height, load cross-

TABLE 1
EXPERIMENTAL PLAN

		Degreaser A			Degreaser B	
	Test No.	Exp. No.	Description	Test No.	Exp. No.	
PHASE I - 1,1,1-trichlorethane	1	1A 2A 3A	Idle test, cover open Idle test, cover closed Covering during operation	1	1B 2B 3B	Idle test, cover open Idle test, cover closed No covering in operation
	2	4A 5A 6A 7A 8A 9A 10A 11A	Variables:* FB = 50/125% SC = on/off A = 50/70% V = 8 ft/min	2	4B 5B 6B 7B 8B 9B 10B 11B	Variables: FB = 50/125% SC = on/off A = 50/70% V = 8 ft/min
	3	12A 13A 14A 15A	Variables: V = 16 ft/min FB = 50/125% A = 50/70% SC = off	4	12B 13B 14B 15B	Variables: FB = 75/100% V = 8/16 ft/min A = 50% SC = off
	5	16A 17A	Variables: FB = 75/100% V = 8 ft/min SC = off	5	16B 17B	Variables: Small degreaser[b] FB = 75% V = 8 ft/min A = 50% SC = off
PHASE II - Methylene chloride	1	18A 19A 20A 21A 22A 23A 24A 25A	Variables: FB = 50/125% SC = on/off A = 50/70% V = 8 ft/min	1	18B 19B 20B 21B 22B 23B 24B 25B	Variables: FB = 50/125% SC = on/off A = 50/70% V = 8 ft/min
	2	26A 27A	Variables: FB = 75% A = 50% V = 8 ft/min SC = off Exhaust = 50/100 ft/min	3	26B	Cross-current test

* FB— Freeboard height.
SC—Secondary condenser.
A- Load cross-sectional area.
V—Hoist speed.
[b] Small degreaser will be used for this experiment.

sectional area, refrigeration freeboard chiller, hoist speed, and degreaser size.

DEGREASER OPERATION

During the tests the degreasers are operated continuously under different conditions for a preset time period for each experiment. All experiments in this test program are run for 24 hours to determine any significant differences in solvent consumption at each level of a variable being tested. During this time period, the load is cleaned continuously over a preset cycle. Scales with a 113.4g (0.25 pound) precision are used to measure the total solvent consumption. Thus for a 9Kg (20-pound) loss in solvent, a maximum error of 1.25 percent could occur. The error limit becomes smaller with higher solvent consumption rates and longer experimental periods.

A well defined clean load consisting of an extra heavy wall black iron pipe coil, 8.5m (28 feet) long and weighing 45.4 Kg (100 pounds), is used for each degreaser. The load is placed on a perforated metal sheet placed in a 22.6 Kg (50 pound) basket. To decrease cycle time, the load is designed to be rapidly water cooled after each degreasing cycle.

During the experimental period for most of the tests, the load is operated continuously. During operation so far, typical cycle time has been about 6.5 minutes. Table 2 presents an approximate cycle time distribution.

Parameters that are measured periodically during each test are solvent consumption, solvent concentration over the degreaser, temperature, humidity, air flow, and barometric pressure. Cooling water rates and temperature, and electrical consumption are also measured periodically during the test. Solvent consumption is the most important parameter because the effect of design and operating variables will be compared to consumption.

TEST RESULTS

Tests conducted so far have been run to determine the effect of freeboard height, load area, and the utilization of covers on solvent emissions. Figures 1 to 5 present the results in terms of emission rate from the two degreasers A and B. These tests were conducted over 8 to 24 hour periods without secondary chillers and using 1,1,1-trichloroethane solvent. The load was cleaned
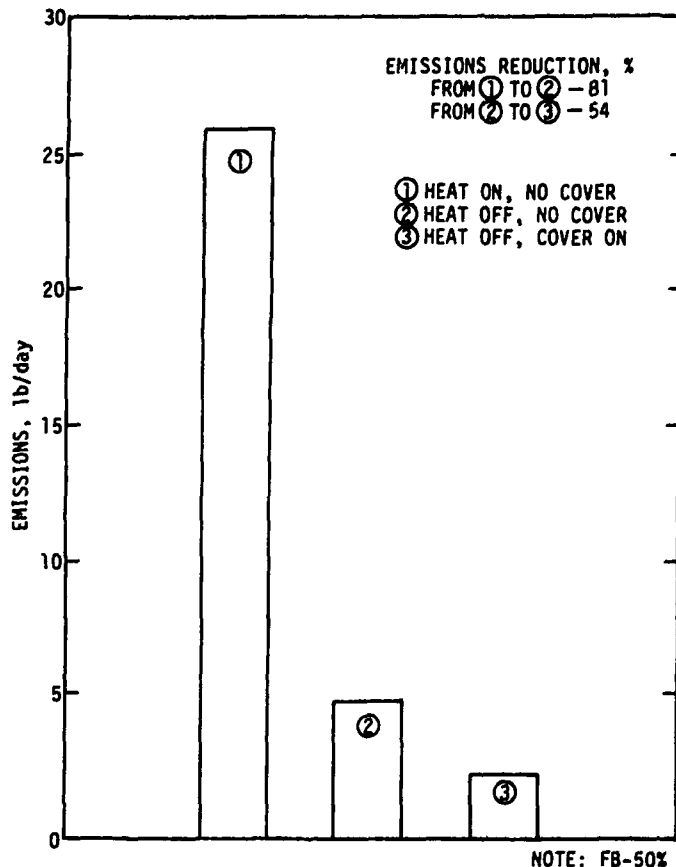

Fig. 1—Emissions from idling degreaser.

Fig. 2—Solvent emissions from degreaser at different freeboard heights and load size (A) at 50 percent ratio.

TABLE 2
TYPICAL CYCLE TIME DISTRIBUTION

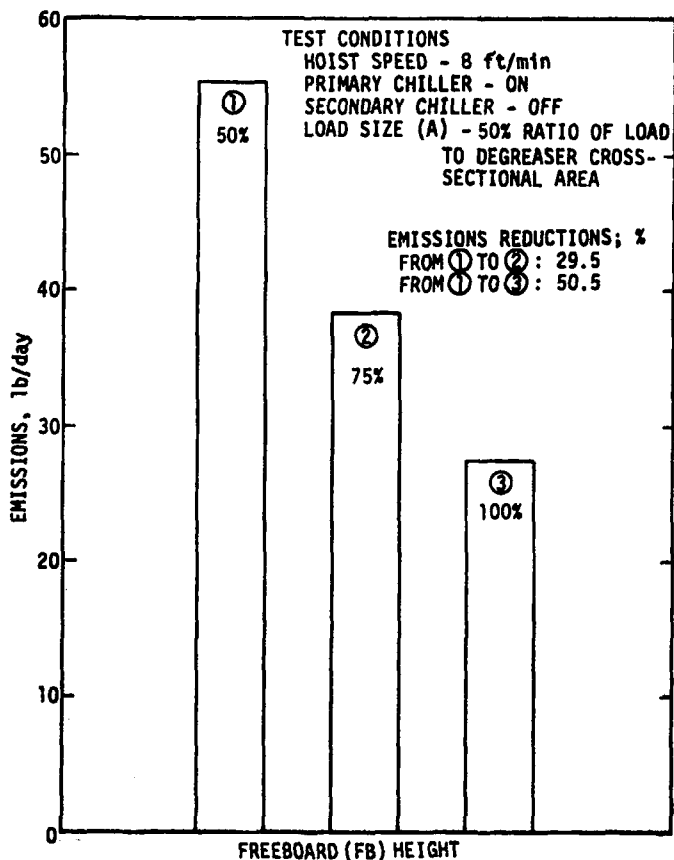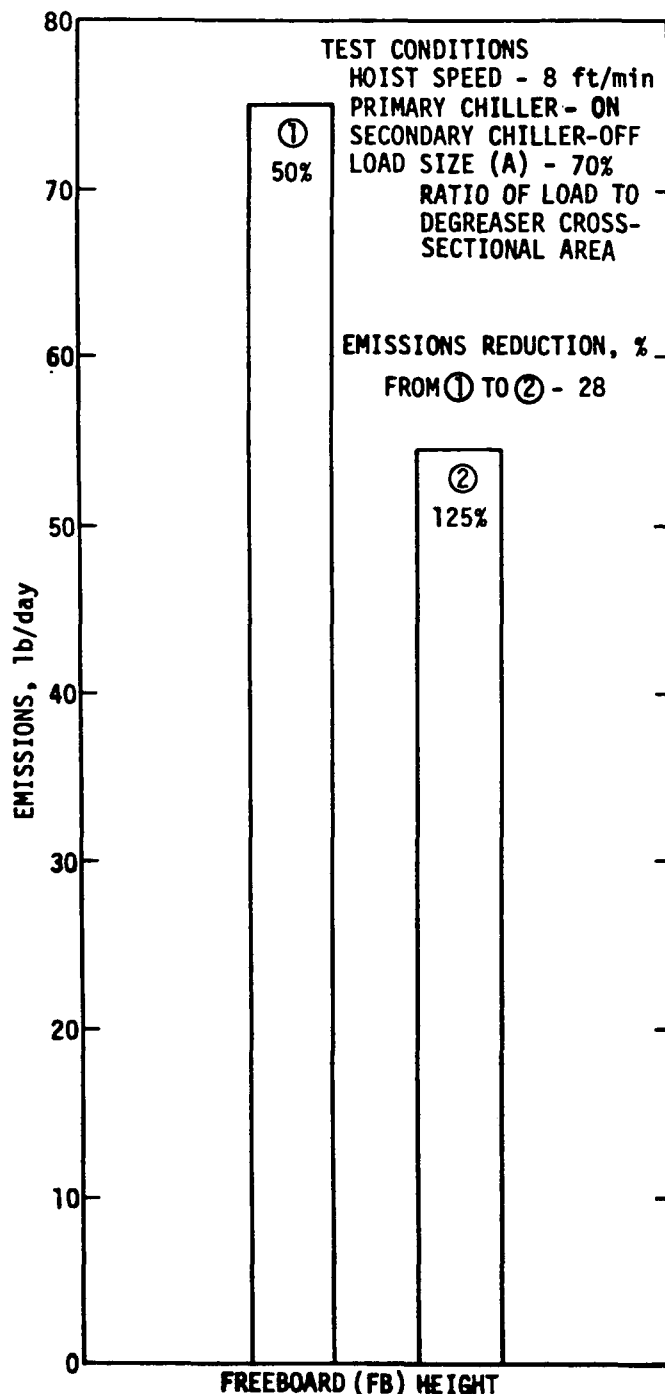| Time Interval	Action
30 seconds	load descent
3 minutes & 30 seconds	load cleaning
30 seconds	load ascent
20 seconds	pause
60 seconds	load cooling
15 seconds	air flushing of load
25 seconds	pause

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Fig. 3—Solvent emissions from degreaser at different freeboard heights and load size (A) at 70 percent ratio.

Fig. 4—Effect of load size on degreaser emissions.

continuously (6.5 minutes per cycle) at a hoist speed of 2.6m (8 feet per minute).

Figure 1 presents data on solvent loss from an idling degreaser with a freeboard height of 50 percent. Covering the degreaser top decreased the solvent emissions by 54 percent when no heat was applied. Boiling solvent in an open top degreaser with no cover increased emissions by 81 percent.

Figure 2 and 3 show the effectiveness of increased freeboard height on degreasers cleaning normal size (50% area ratio) and oversize load (70% area ratio),
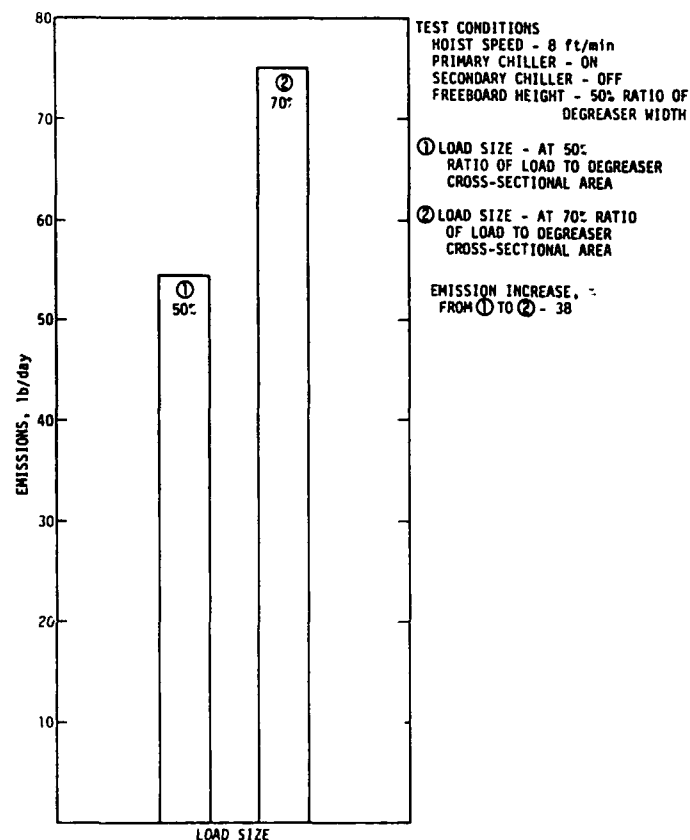
respectively. The degreaser cleaning normal size loads emitted about 30 percent less solvent when the freeboard height increased from 50 to 75 percent, and about 50 percent less solvent when the freeboard height doubled from 50 to 100 percent of degreaser width. The degreaser cleaning oversize loads emitted about 29 percent less solvent when the freeboard height increased from 50 to 125 percent.

As shown in Figure 4, oversize load cleaning increased emissions by 38 percent at a 50 percent freeboard height.

Figure 5 is an indication of cover usage on emission rates. However, the data may not represent the effectiveness of cover usage. During the tests on the degreaser with no cover, the load was cleaned continuously, but the other degreaser was kept closed with periodic opening every half hour for one load cleaning. The net result was the total amount of work cleaned during the later test was only 30 percent of that cleaned with the open degreasers. Thus, emissions on a unit of load cleaned basis were actually less with the cover off.

CONCLUSIONS

Test data produced thus far indicate substantial savings in solvent usage with increased freeboard heights and with load size that does not exceed 50 percent of the degreaser open area.

Figure 6 presents solvent cost savings from degreasers cleaning normal size loads. An increase of freeboard height from 50 to 75 percent resulted in solvent savings of
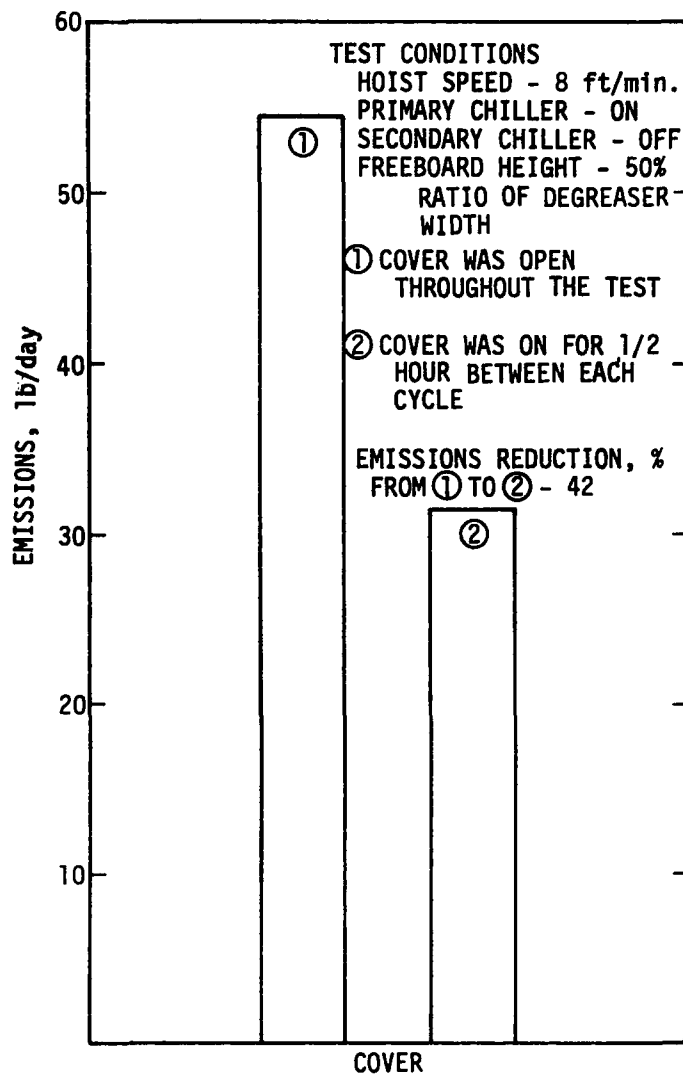
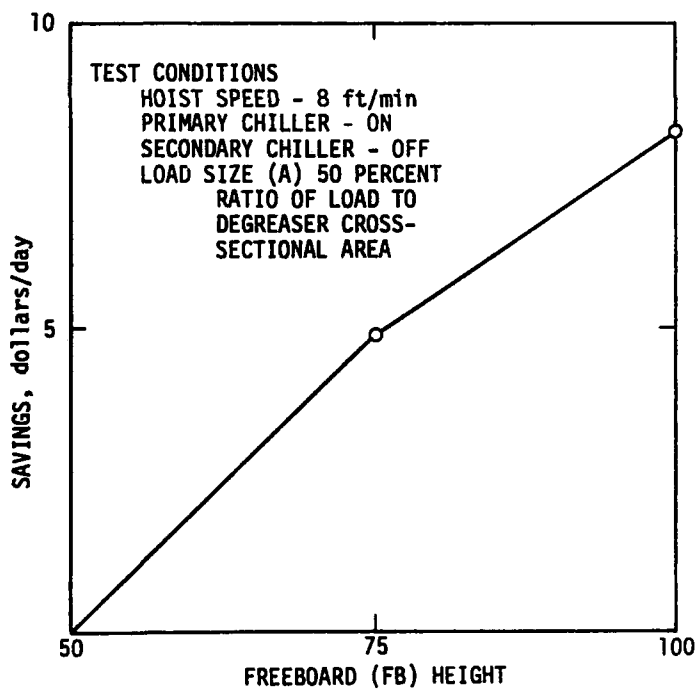## Fig. 5 — Effect of cover usage on degreaser emissions

EMISSIONS, lb/day

TEST CONDITIONS
HOIST SPEED - 8 ft/min.
PRIMARY CHILLER - ON
SECONDARY CHILLER - OFF
FREEBOARD HEIGHT - 50%
RATIO OF DEGREASER WIDTH

① COVER WAS OPEN THROUGHOUT THE TEST

② COVER WAS ON FOR 1/2 HOUR BETWEEN EACH CYCLE

EMISSIONS REDUCTION, % FROM ① TO ② - 42

COVER

Fig. 5—Effect of cover usage on degreaser emissions.

Fig. 6

SAVINGS, dollars/day

TEST CONDITIONS
HOIST SPEED - 8 ft/min
PRIMARY CHILLER - ON
SECONDARY CHILLER - OFF
LOAD SIZE (A) 50 PERCENT
RATIO OF LOAD TO
DEGREASER CROSS-
SECTIONAL AREA

FREEBOARD (FB) HEIGHT

Fig. 6—Solvent cost saving with freeboard height.

Fig. 7

SAVINGS, dollars/day

A=50

A=50

A=70

TEST CONDITIONS
HOIST SPEED - 8 ft/min
PRIMARY CHILLER - on
SECONDARY CHILLER - OFF
A - RATIO OF LOAD TO
DEGREASER CROSS-
SECTIONAL AREA

FREEBOARD (FB) HEIGHT
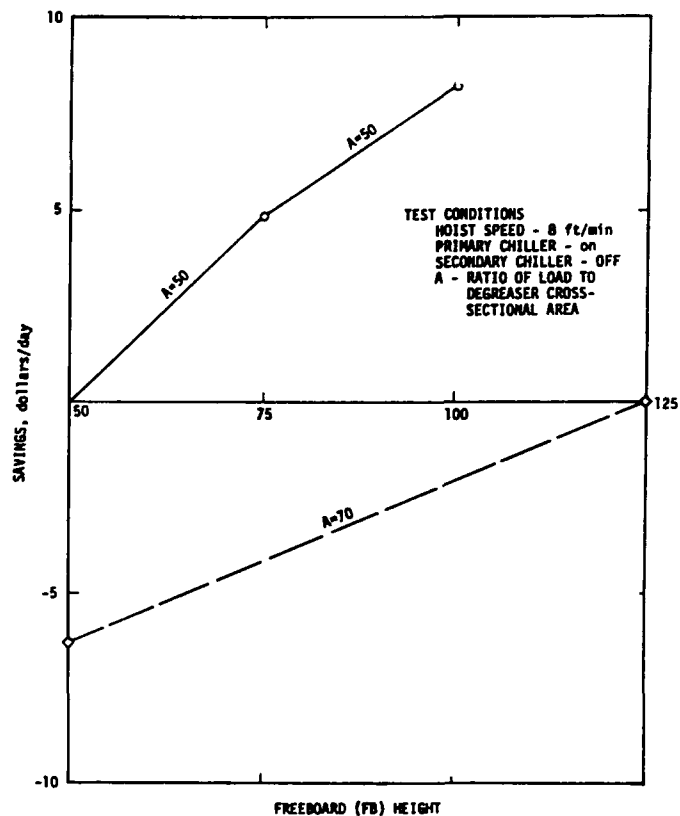
Fig. 7—Solvent cost savings with load-size and freeboard height.

Fig. 8

COST OF SOLVENT LOSS FROM DEGREASER TOP, dollars/day

TEST CONDITIONS
HOIST SPEED - 8 ft/min
PRIMARY CHILLER - ON
SECONDARY CHILLER - OFF
A = LOAD SIZE, %
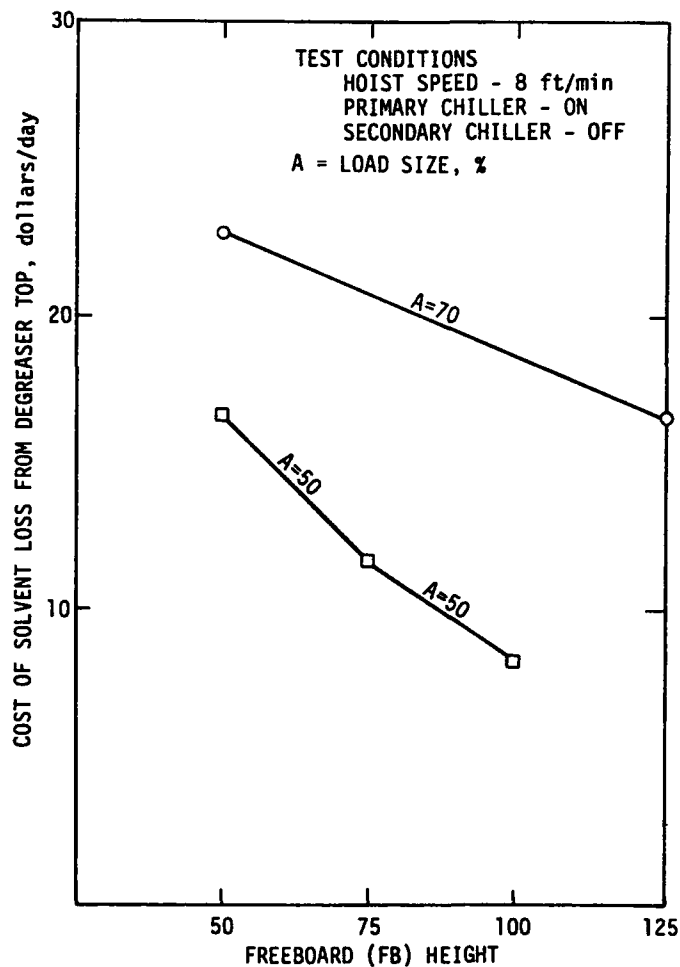
A=70

A=50

A=50

FREEBOARD (FB) HEIGHT

Fig. 8—Cost of solvent loss from degreaser.

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$4.83 per day and an increase from 50 to 100 percent resulted in savings of $8.72 per day.

As shown in Figure 7, oversize load cleaning resulted in additional costs of $6.23 per day. The degreaser required a 125 percent freeboard height to off-set the additional cost due to oversize load cleaning.

The results indicate that cleaning a normal size load in a degreaser using increased freeboard height is more economical as shown in Figure 8.

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16. ABSTRACT

Subject report contains technical research papers given at the Second Conference on Advanced Pollution Control for the Metal Finishing Industry. This conference was held in February, 1979 and was co-sponsored by the USEPA and the American Electroplaters' Society (AES). Report contains papers on IERL-Ci research efforts and covers all facets of air, water, and solid waste pollution control.

17. KEY WORDS AND DOCUMENT ANALYSIS

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