



Project Summary

Cadmium and Chromium Recovery from Electroplating Rinsewaters

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This evaluation addresses the product quality, pollution prevention potential, and economic factors involved in the use of ion exchange to recover cadmium and chromium from electroplating rinsewaters and to remove contaminants for reuse of rinsewater. Cadmium, chromium, and cyanide (which is part of the cadmium bath) are on EPA's 33/50 list of target chemicals. Test results showed that the water returned to the rinse after ion exchange was of acceptable quality for both the cadmium and chromium processes. The ion exchange resins are regenerated with sodium hydroxide (NaOH). On the cadmium line, the regenerant was subjected to electrolytic metal recovery (EMR) to recover cadmium for reuse in the plating bath. On the chromium line, the regenerant was passed through a cation exchange resin in an effort to recover chromic acid. Although the recovery results were good on the cadmium line, chromic acid could not be recovered in this test. The pollution prevention potential of ion exchange on the cadmium and chromium rinsewater is good; however, further testing is needed to establish good recovery of chromium as chromic acid from the regenerant. The ion-exchange processes also proved economically viable.

This Project Summary was developed by the U.S. EPA's Risk Reduction Engineering Laboratory (RREL), Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same

title (see Project Report ordering information at back).

Introduction

This study, performed under the U.S. EPA Waste Reduction and Innovative Technology Evaluation (WRITE) Program, was a cooperative effort among EPA's RREL, the Connecticut Hazardous Waste Management Service, and the Torrington Company. The objective of the WRITE Program is to evaluate, in a typical workplace environment, examples of prototype or innovative commercial technologies that have potential for reducing waste. The ion exchange system used in this study was manufactured by CTEO Tek, Inc.* and supplied by Plating Services, Inc. Other ion exchange units and technologies applicable to the same wastestream (electroplating rinsewaters) are also commercially available.

The objectives of this study were to evaluate (1) the effectiveness of the ion exchange unit in cleaning the rinsewater for reuse in the rinse tanks, (2) the pollution prevention potential of this technology, and (3) the cost of ion exchange versus the cost of the former practice (disposal).

Figure 1 shows the cadmium ion exchange system configuration. The water from Rinse 1 tank is first passed through a filter to prevent suspended solids from contacting the resin in the ion exchange column. The anionic resin captures the cadmium-cyanide complex, and the water

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.



is returned to the Rinse 2 tank. An emergency bypass valve allows this water to be discharged to waste in case cadmium or cyanide levels are found to be too high.

The resin is periodically regenerated with a 15 to 20% NaOH solution, and the regenerant is taken to the electrolytic metal recovery (EMR) unit, where cadmium is recovered on the cathode and returned to the plating tank. Some cyanide is destroyed by decomposition during the EMR process.

Figure 2 shows the chromium system configuration. The primary ion exchange resin is anionic to remove hexavalent chrome. In the future, a cationic resin component will be added to the primary resin to remove any trivalent chrome that may

be present in the rinsewater. The anionic resin is also regenerated with a 15 to 20% NaOH solution. The resulting solution (sodium chromate) is run through a secondary (cationic) exchange unit that should convert the regenerant back to chromic acid and return it to the plating tank.

Product Quality Evaluation

The objective of this part of the evaluation was to show that water processed through the ion exchange system is clean enough for use as rinsewater in the cadmium or chromium plating lines. Contaminant-free rinsewater ensures a good workpiece finish. The approach was to collect three samples each of the rinsewater, before and after passing

through the ion exchange system. These samples were analyzed in the laboratory to evaluate the removal of contaminants. In addition, batches of rinsewater (one batch for cadmium and one for chromium) were spiked with plating bath solution to elevate contaminant levels (cadmium or chromium), and the spiked rinsewater was run through the ion exchange to test the limits of the unit. Because rinsewater was continuously circulated through the ion exchange system during the day, three samples of the rinsewater — at the beginning, middle, and end of a shift — were taken to ensure that water quality remained relatively steady over time.

Table 1 presents the results of the laboratory analysis of the cadmium rinsewater

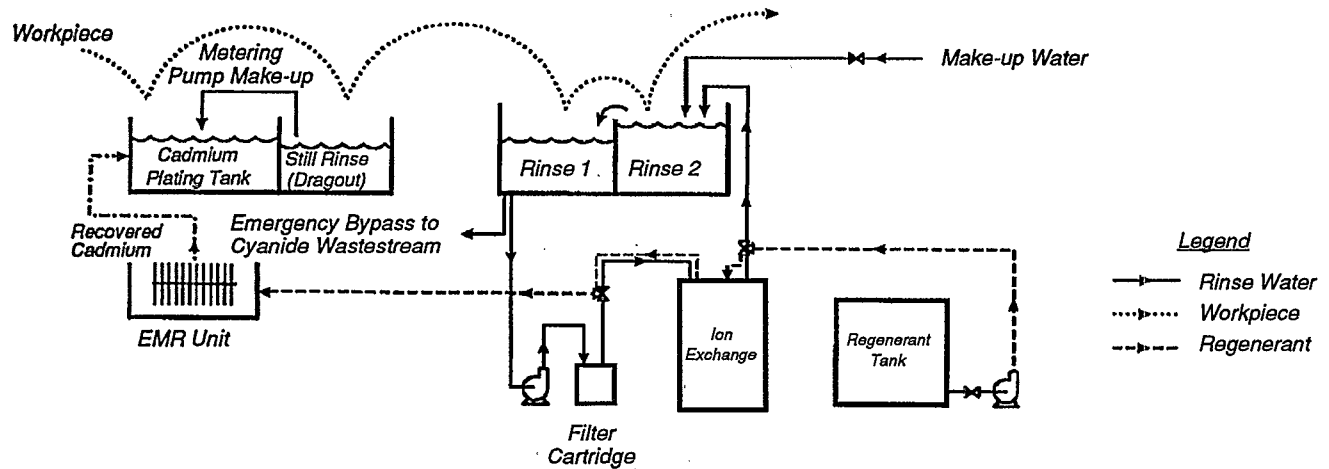


Figure 1. Ion exchange recovery of cadmium from plating rinsewater.

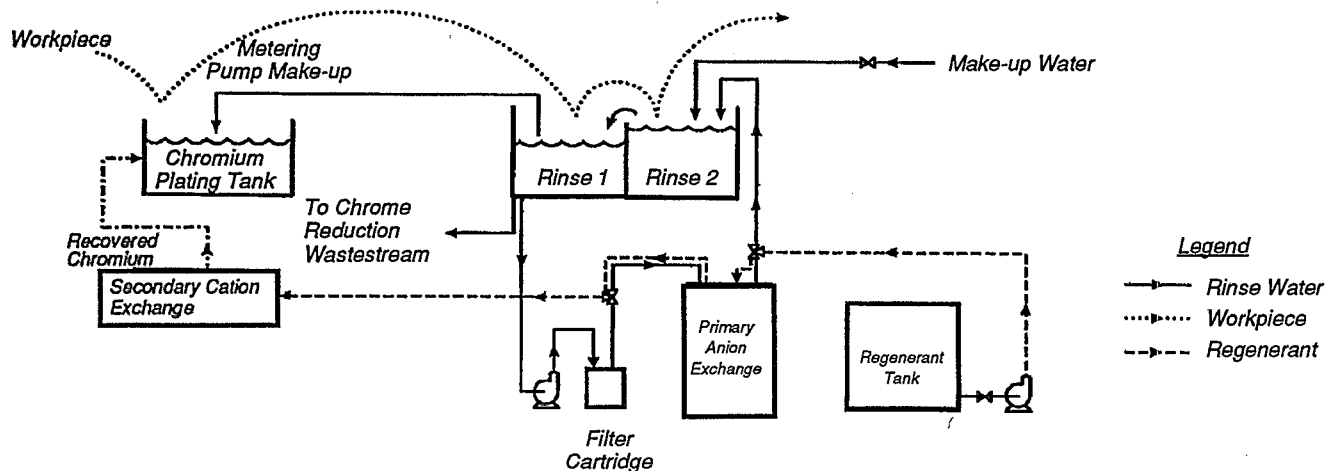


Figure 2. Ion exchange recovery of chromium from plating rinsewater.

Table 1. Cadmium Rinsewater Analysis

Sample No.	Sample Description	pH	Conductivity (umhos/cm)	Cadmium (mg/L)	Cyanide (mg/L)	Iron (mg/L)	Dissolved Solids (mg/L)	Suspended Solids (mg/L)
CD-X1-B1	Before ion-x, Run 1	11.26	783	7.28	35.60	0.57	226	1
CD-X1-B2	Before ion-x, Run 2	11.41	864	2.23	9.26	0.22	196	< 1
CD-X1-B3	Before ion-x, Run 3	11.48	936	2.58	13.80	0.31	205	< 1
CD-X1-A1	After ion-x, Run 1	11.45	867	0.015	0.037	0.06	147	< 1
CD-X1-A2	After ion-x, Run 2	11.51	845	<0.01	0.047	0.06	161	2
CD-X1-A3	After ion-x, Run 3	11.51	885	0.01	0.041	0.02	163	< 1
CD-XS-B1	Spike, before ion-x	NA ^(a)	NA	38.7	117	NA	NA	NA
CD-XS-A1	Spike, after ion-x	NA	NA	3.69	14.6	NA	NA	NA
CD-R1-B1	Rinse 1, 9:00 am	10.72	278	1.80	8.55	0.28	90	1
CD-R1-B2	Rinse 1, 12:30 pm	11.37	823	3.55	15.60	0.34	190	< 1
CD-R1-B3	Rinse 1, 4:00 pm	11.40	985	4.71	24.70	0.41	225	10
CD-R2-B1	Rinse 2, 9:00 am	11.07	360	0.067	0.28	0.11	80	2
CD-R2-B2	Rinse 2, 12:30 pm	11.50	860	0.105	0.62	0.07	164	3
CD-R2-B3	Rinse 2, 4:00 pm	11.47	970	0.269	1.23	0.09	191	< 1
CD-X30-B1	Rinse 1, 30-min	11.35	760	4.31	17.60	0.33	189	3
CD-FB-1	Field blank	7.50	65.3	<0.01	<0.01	0.21	50	1

(a) NA = not analyzed.

samples. Most of the cadmium and cyanide were removed by ion exchange — in some cases, to below detection levels. The pH of the rinsewater remained steady at alkaline levels throughout the testing.

A statistical t-test (95% significance level) was performed based on the averages and standard deviations of the 1-min "before" and "after" (CD-X1-) data. Suspended solids levels were very low in both "before" and "after" samples. After ion exchange, concentrations of cadmium, cyanide, and iron in the rinsewater decreased significantly. Overall dissolved solids levels also showed a significant decrease after ion exchange; this indicated a decline in dissolved mass levels. Interestingly, conductivity did not show any significant change after ion exchange, indicating that the current-carrying capacity of the rinsewater did not change. During ion exchange, heavier ions (cadmium, iron, etc.) transfer to the resin and lighter sodium ions are transferred to the water. Thus, dissolved mass in the water decreases but conductivity remains relatively constant. Small amounts of fresh makeup water were added to the rinsewater loop from time to time to compensate for the water lost to evaporation and dragout with the parts; this also helped control conductivity.

Table 2 describes the results of the laboratory analysis of the chromium

rinsewater samples. After ion exchange, the rinsewater pH levels were slightly alkaline (9.31 to 9.45) because chromate ions (and any other contaminant anions) had been substituted with hydroxide ions. The alkaline pH was neutralized in the rinse tanks by the chromic acid residue on the parts (workpiece).

Similar statistical analyses were performed on the chromium data as have been described for the cadmium data. Suspended solids levels were significantly reduced by the cartridge filter ahead of the resin. Chromium (total chromium) and iron levels decreased significantly after ion exchange. Iron removal may be due either to removal of ferrous suspended particles on the cartridge filter or to deposition of complexed iron on the resin. As in the cadmium tests, dissolved solids mass decreased significantly, but conductivity (current-carrying strength) remained constant after ion exchange. This is because heavier chromates in the rinsewater were replaced with lighter hydroxide ions.

Pollution Prevention Evaluation

The pollution prevention potential of the ion exchange technology was assessed in terms of waste volume reduction and pollutant reduction. Waste volume reduction addresses the gross wastestream (e.g., lb of wastewater treatment sludge) and affects environmental resources (e.g.,

landfill space) expended through disposal. Pollutant reduction addresses the specific pollutants in the wastestream (e.g., chromium in the sludge).

Table 3 summarizes the waste volume reduction. By using ion exchange, large volumes of water are saved from going to waste. This water (an important resource) can be reused as a rinse on the cadmium and chromium lines. Without ion exchange, Torrington must maintain high rinsewater flow rates (8 gpm for the cadmium line and 2 gpm for the chromium line). These continuous flows generate large amounts of wastewater that have to be treated on site. With the ion exchange system on the cadmium line, Torrington requires only 50 gal/day to make up for dragout losses. A similar makeup rate is expected on the chromium line. Therefore, with the addition of the ion-exchange system, the amount of wastewater that must be treated is reduced. Virtually eliminating the wastewater stream also eliminates the hazardous sludge (containing cadmium or chromium) that has to be handled, transported, and disposed.

In terms of pollutant reduction on the cadmium line, the pollutants of interest are cadmium and cyanide. Before ion exchange, cadmium in the rinsewater was lost to wastewater, which was sent to an on-site wastewater treatment plant. The wastewater was treated in a steel cyanide

Table 2. Chromium Rinsewater Analysis

Sample No.	Sample Description	pH	Conductivity (umhos/cm)	Total Chromium (mg/L)	Iron (mg/L)	Dissolved Solids (mg/L)	Suspended Solids (mg/L)
CR-X1-B1	Before ion-x, Run 1	4.83	103	20.0	0.90	93	9
CR-X1-B2	Before ion-x, Run 2	4.67	104	18.2	0.85	99	8
CR-X1-B3	Before ion-x, Run 3	4.41	106	21.3	0.87	106	6
CR-X1-A1	After ion-x, Run 1	9.38	198	0.048	0.15	96	< 1
CR-X1-A2	After ion-x, Run 2	9.31	126	0.111	0.20	70	< 1
CR-X1-A3	After ion-x, Run 3	9.45	115	0.271	0.26	71	< 1
CR-XS-B1	Spike, before ion-x	NA(a)	NA	33.6	NA	NA	NA
CR-XS-A2	Spike, after ion-x	NA	NA	0.294	NA	NA	NA
CR-X2-B1	Rinse 1, 30-min	4.68	105	19.9	0.73	87	2
CR-FB-1	Field blank	7.50	65.3	0.04	0.21	50	1

(a) NA = Not analyzed.

Table 3. Waste Volume Reduction

<u>Without Ion Exchange</u>		<u>With Ion Exchange</u>	
Waste Description	Amount Generated per Year ^(a)	Waste Description	Amount Generated per Year ^(b)
Cadmium System Wastewater	1,920,000 gal	Wastewater Regenerant Filter cartridges	0 gal 660 gal 6
Chromium System Wastewater	480,000 gal	Wastewater Regenerant Filter cartridges	0 gal 840 gal 12

(a) Based on values of 16 hr/day, 5 days/wk, 50 wk/yr.

(b) Based on pilot tests conducted by the Torrington Company and resin capacity.

treatment tank using chlorine gas, sodium hypochlorite, calcium hypochlorite, and NaOH to oxidize the cyanide. The cadmium and other metals formed hydroxides that settled in the clarifier as sludge, which was then hauled off site for disposal. The treated water was discharged to the municipal sewer under a permit.

At Torrington, prior to ion exchange, approximately 69 lb of cadmium and 281 lb of cyanide were discharged annually. Now, because most of the cadmium can be recovered and reused, this pollutant is virtually eliminated from the wastestream. Some cyanide is also destroyed in the cadmium recovery process.

On the chromium line, without ion exchange, approximately 80 lb of chromium is discharged annually. With ion exchange, most of the chromium will be captured on the resin, which will be regenerated with

NaOH. The regenerant then will pass through a cation exchange resin for conversion of sodium chromate to chromic acid. However, when this recovery was performed during the pilot unit testing, the final regenerant liquid still showed a pH of 13.08. This indicates that sodium chromate had not been converted to chromic acid; if it had been, the pH would have been much lower. This may be because (a) an excess of NaOH was used to regenerate the resin and/or (b) insufficient resin was available to exchange all the sodium in the regenerant. Further testing is needed to determine the feasibility of the chromic acid recovery process.

Economic Evaluation

The economic evaluation involves comparing the costs of the ion exchange operation with those of the former practice

(counterflow rinse). These comparisons are summarized in Tables 4 and 5. Operating costs for ion exchange recovery are much lower than those for counterflow rinse alone. The main cost saving is the reduction in wastewater treatment costs.

In addition to operating cost savings, the recovered cadmium has value because it is reused in the plating bath as a cadmium anode. The cost of cadmium anodes is approximately \$15/lb. The resulting value of the 69 lb/yr of recovered cadmium is approximately \$1,036/yr.

The chromium deposited on the ion exchange resin also has value if it can be successfully recovered as chromic acid. The cost of chromic acid is approximately \$2.50/lb. Approximately 80 lb/yr of chromium metal is deposited on the ion exchange resin. This corresponds to about 154 lb of chromic acid (CrO₃). However, further testing is needed to establish the feasibility of chromic acid recovery from the chromium in the regenerant.

The purchase price of the cadmium ion exchange system was \$8,100 (including ion exchange resin column, pumps, and collection tanks). The EMR equipment price was \$4,125 (including rectifier, pump, anodes, cathodes, and solution tank). Installation cost at Torrington, including materials (piping, etc.) and labor, was approximately \$3,500, to which \$5,000 was added to approximate the cost of in-house pilot testing to determine specifications for the individual plant.

The purchase price of the chromium ion exchange system is estimated to be \$8,200 (including ion exchange resin column, pumps, and tanks). Installation cost at Torrington is expected to be \$3,500, including materials (piping, etc.) and labor.

Table 4. Operating Costs Comparison for Cadmium System

Item	Amount Used per Year	Unit Cost	Total Annual Cost
<i>Without Ion Exchange</i>			
Freshwater	1,920,000 gal	\$ 0.70/1000 gal	\$ 1,344
Wastewater treatment	1,920,000 gal	\$ 22/1000 gal	\$ 42,240
		<i>Total</i>	<i>\$ 43,584</i>
<i>With Ion Exchange</i>			
Freshwater	12,500 gal	\$ 0.70/1000 gal	\$ 9
Chemicals (50% NaOH)	96 gal	\$ 1.50/gal	\$ 144
Energy	1564 kW hr	\$ 0.075/kW hr	\$ 117
Labor	173 hr	\$ 7/hr	\$ 1,211
<i>Routine maintenance</i>			
- filter cartridges	6	\$ 5	\$ 30
- EMR anode plates	1	\$ 30	\$ 30
- EMR cathode plates	12	\$ 30	\$ 360
- labor	24 hr	\$ 7/hr	\$ 168
<i>Waste Disposal</i>			
- regenerant	660 gal	\$ 22/1000 gal	\$ 15
- filters	6	\$ 400/36 units	\$ 67
		<i>Total</i>	<i>\$ 2,151</i>

Table 5. Operating Costs Comparison for Chromium System

Item	Amount Used per Year	Unit Cost	Total Annual Cost
<i>Without Ion Exchange</i>			
Freshwater	480,000 gal	\$ 0.70/1000 gal	\$ 336
Wastewater treatment	480,000 gal	\$ 15/1000 gal	\$ 7,200
		<i>Total</i>	<i>\$ 7,536</i>
<i>With Ion Exchange</i>			
Freshwater	12,500 gal	\$ 0.70/1000 gal	\$ 9
Chemicals (50% NaOH)	240 gal	\$ 1.50/gal	\$ 360
Energy	1492 kW hr	0.075/kW hr	\$ 112
Labor	149 hr	\$ 7/hr	\$ 1,043
<i>Routine maintenance</i>			
- filters	12	\$ 5	\$ 60
- labor	24	\$ 7/hr	\$ 168
<i>Waste Disposal</i>			
- regenerant	840 gal	\$ 15/1000 gal	\$ 13
- filters	6	\$ 400/36 units	\$ 67
		<i>Total</i>	<i>\$ 1,832</i>

The approximate cost of \$5,000 for in-house testing was also added for this unit.

A rough estimate of the payback period can be obtained by the following formula:

$$\text{Payback, years} = \frac{\text{capital costs}}{\text{operating cost savings} + \text{recovery value}}$$

Therefore, the payback period for the cadmium ion exchange system is less than

1 year. For the chromium system, the payback period is approximately 3 years. Because chromic acid recovery from the regenerant is yet to be established, no recycled chromium value is assumed.

The above payback period estimation is a simple calculation that does not take into account such factors as taxes, depreciation, inflation, etc. A more detailed economic evaluation, based on the worksheets

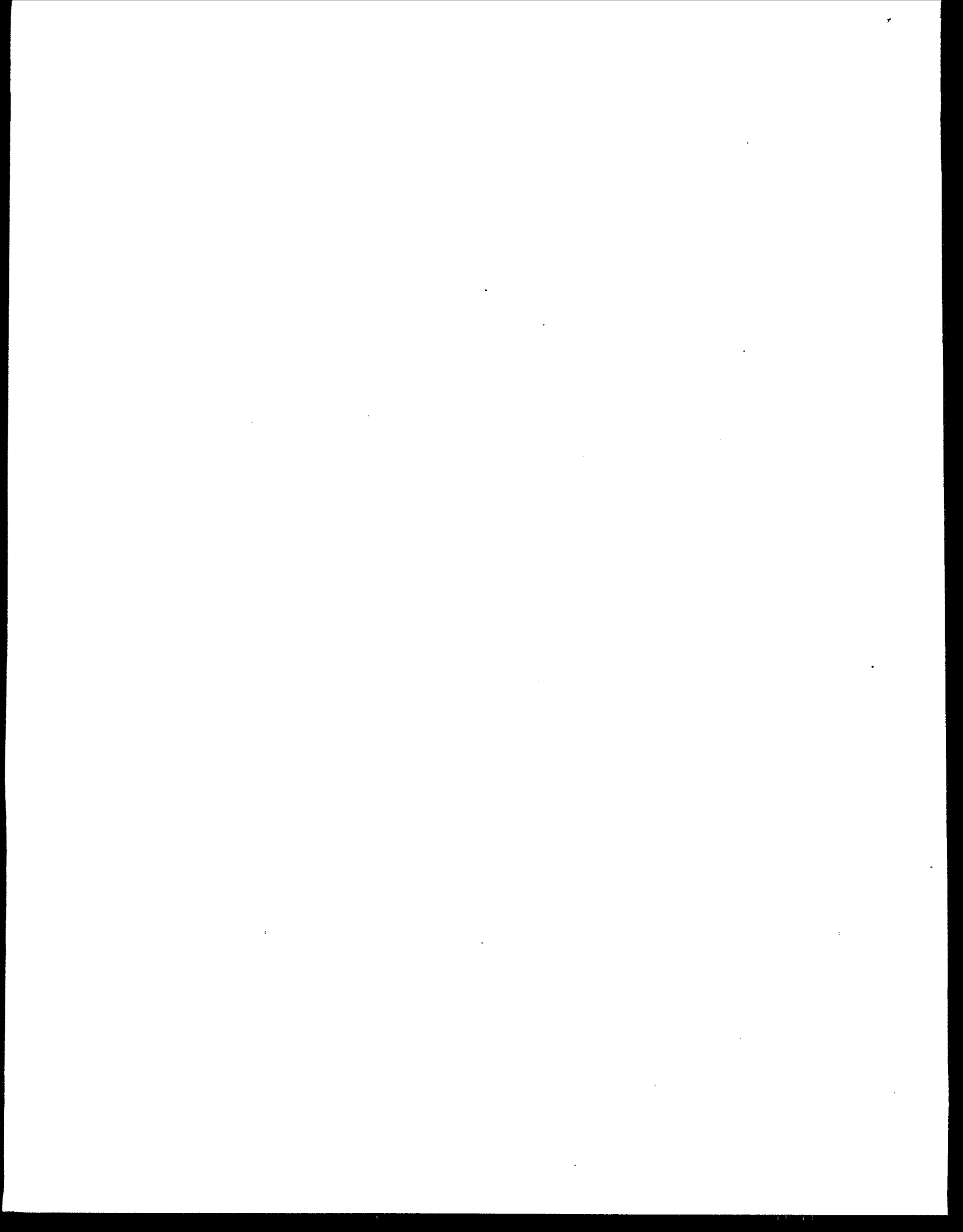
provided in the Facility Pollution Prevention Guide (EPA 600/R-92/088), was performed that took these factors into account. The results showed that, for the cadmium process, the return on investment (with cost of capital equal to 15%) was still less than 1 year. For the chromium process, the return on investment (with cost of capital equal to 15%) was over 5 years. This includes capital costs of engineering and installation as well as increased overhead costs due to addition of the units.

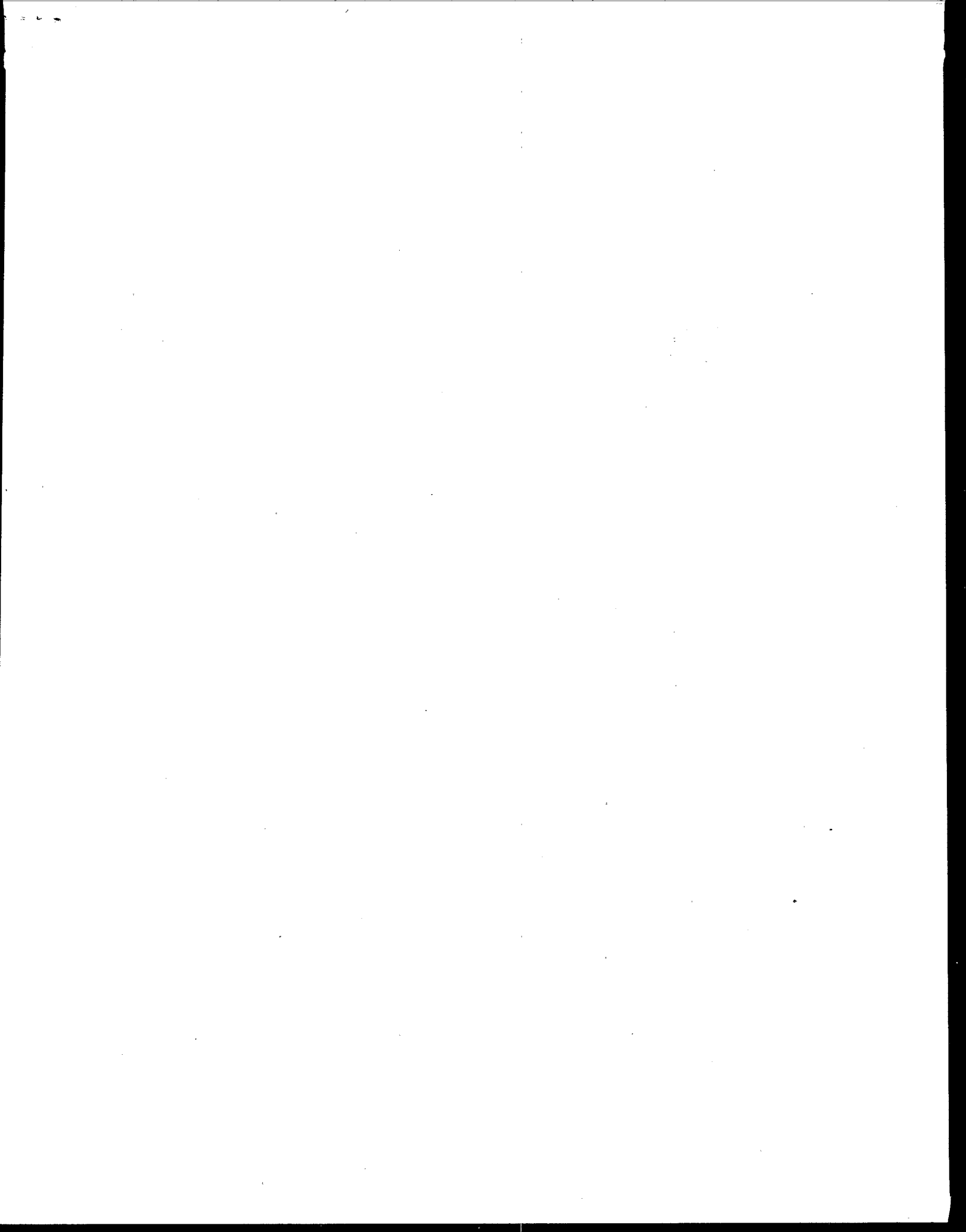
Conclusions and Discussion

The evaluation showed that rinsewater on both cadmium and chromium lines at Torrington Company can be reused after subjecting it to filtration and ion exchange to remove impurities. Large volumes of water are thus saved, and large amounts of hazardous metals sludge are kept from the environment. The sidestreams from ion exchange are negligible compared with the wastewater and sludge wastestreams that are generated in the absence of ion exchange. The ion exchange resin can be regenerated with NaOH. On the cadmium line, the regenerant can be subjected to EMR and the cadmium recovered on the cathode. This electrode, with the deposited cadmium, is then inserted in the plating tank as a cadmium anode. Thus, a hazardous pollutant, cadmium, is reused. On the chromium line, further testing is needed to establish the feasibility of recovering chromium as chromic acid for reuse in the bath.

Without ion exchange, the rinsewater must undergo an expensive wastewater treatment process. The cost of operating the ion exchange unit is more than offset by the savings in wastewater treatment costs and by the value of the recovered product. In addition to the direct economic benefits, the ion exchange system also reduces Torrington Company's potential liability by virtually eliminating the risks involved during off-site transport and disposal of hazardous sludge.

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Lisa Brown is the EPA Project Officer (see below).

The complete report, entitled "Cadmium and Chromium Recovery from Electroplating Rinsewaters," (Order No. PB94-156395; Cost: \$19.50, subject to change) will be available only from:

National Technical Information Service

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