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**Hexavalent Chromium Reduction  
Pretreatment Process Evaluation  
Randolph AFB TX**

**NANCY S. HEDGEcock, 1Lt, USAF, BSC**

**SEPTEMBER 1990**

**Final Report**

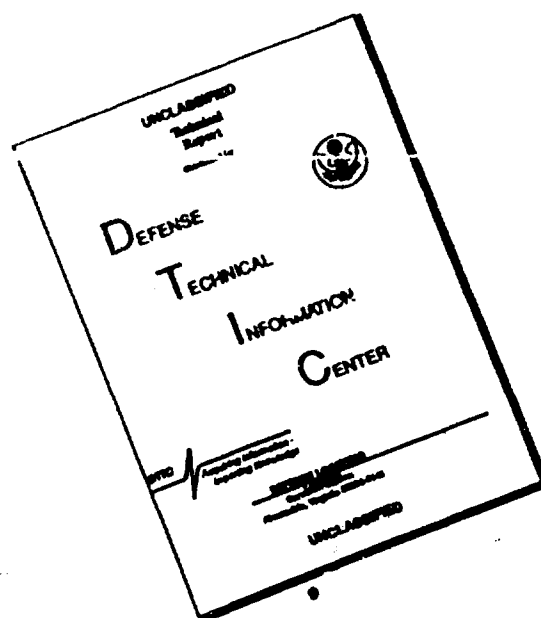
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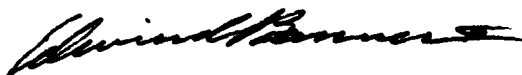
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13. ABSTRACT (Maximum 200 words)  At the request of HQ ATC/SGPB, the AFOEHL conducted a hexavalent chromium reduction pretreatment process evaluation at Randolph AFB (RAFB) on 11 May 90. The scope of this survey was to evaluate an experimental in-situ chromium reduction process. The objective was to determine if base personnel could safely and effectively treat chromium waste so that it would no longer be considered a hazardous waste. Recommendations include: (1) Obtain approval from TWC to perform the pretreatment process; (2) Perform cyanide removal on each drum of waste; (3) Do not mix the precipitate back into solution before discharging the wastewater to the sanitary sewer; (4) Sample and analyze the sludge for hexavalent chromium; (5) Sample an appropriate percentage of the drums to ensure the process routinely works; (6) Pretreatment personnel should always wear protective clothing. (716)				
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# ACKNOWLEDGMENT

The author greatly appreciates the hardwork provided by the entire sampling team during the survey at Randolph AFB. I would also like to thank Capt Shaffer, Chief, Bioenvironmental Engineering, and his staff for performing industrial hygiene monitoring during the survey and 12 FTW/MALE personnel for their assistance during the survey.

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## I. INTRODUCTION

On 2 April 1990, Headquarters Air Training Command (ATC) requested that the Air Force Occupational and Environmental Health Laboratory, Environmental Quality Branch (AFOEHL/EQE) evaluate an experimental in-situ chromium reduction process at Randolph AFB (see Appendix). The objective of the survey was to determine if base personnel could safely and effectively treat the chromium waste so that it would no longer be considered a hazardous waste.

The survey was conducted by Capt Linda B. Albrecht, 1Lt Nancy S. Hegecock, 1Lt Shelia P. Scott, and Amn Christopher Feagin on 11 May 1990.

## II. DISCUSSION

### A. Base Description

Randolph AFB is located in San Antonio, Texas and is the home of the 12th Flying Training Wing, Headquarters ATC, Air Force Recruiting Service, and Air Force Manpower and Personnel Center.

### B. Background

Prior to 1990, Randolph AFB Corrosion Control personnel stripped paint from aircraft using methylene chloride. The stripper was rinsed from the aircraft using copious amounts of water and discharged to the sanitary sewer. After stripping, the aircraft was treated with alodine (50% chromic acid) to prime the aluminum surface for painting. The process rinsewater was discharged to the sanitary sewer. Later, Corrosion Control personnel began collecting and drumming the waste methylene chloride, alodine, and rinsewater. This procedure produced 700 drums of hazardous waste in a very short time.

To eliminate the methylene chloride from the wastestream, all aircraft are now stripped using plastic bead blasting. However, the alodine treatment waste is still a hazardous waste due to hexavalent chromium concentrations. The base is in the process of purchasing (within the year) an alodine pretreatment process. The pretreatment process will reduce the hexavalent chromium to trivalent chromium. The waste can then be discharged to the sanitary sewer.

During the interim, 12 FTW/MALE has devised an in-situ treatment process to reduce the hexavalent chromium in the alodine treatment waste to trivalent chromium. Trivalent chromium is not a regulated hazardous waste.

### C. In-situ Treatment Process

Randolph AFB Corrosion Control personnel strip paint from aircraft using plastic media blasting. The stripped planes are then treated with alodine to prime the aluminum surfaces for painting. The alodine waste is put into 55-gallon drums for pretreatment.



Cyanide removal is performed by adding approximately 10 ml Clorox bleach to the drum contents and bubbling the solution for 10 minutes before beginning the chromium pretreatment process.

The chromium pretreatment process is as follows:

1. An air bubbling device is placed in the drum and connected to an air line.
2. Sulfuric acid is added until a pH of 2 is reached (hexavalent chromium is reduced to trivalent chromium).
3. Sodium bisulfite is added to the solution forming chromium hydroxide.
4. Sodium hydroxide is added to raise the pH to 10 (causing the chromium hydroxide to flocculate and settle to the bottom of the drum).

After the pretreatment process, the resulting wastewater is pumped through a sand filter and discharged to the sanitary sewer. The base plans to dispose of the sludge as hazardous waste.

#### D. Survey Procedures

Ten drums were selected for a pretreatment process trial run. The drums were numbered 1-10. Drums 1, 2, and 4 contained chromium trioxide. Drums 3, 5, 6, and 10 contained alodine waste. Drums 7, 8, and 9 contained alodine mixed with methylene chloride (from the old stripping process). Pretreatment was not attempted on drums 7, 8, or 9. Samples were taken from each drum using a composite liquid waste sampler (COLIWASA) before and after pretreatment (see Figure). The samples were analyzed for cyanide, total chromium, and hexavalent chromium. Analyses were performed at AFOEHL. Table 1 contains the analytical and preservation methods used.

TABLE 1. ANALYSIS AND PRESERVATION METHODS

Analysis	Preservation	Method
Cyanide	H <sub>2</sub> S	A412D
Total Chromium	HNO <sub>3</sub>	E218
Hexavalent Chromium	HNO <sub>3</sub>	A312A

Note: A - Standard Methods for the Evaluation of Water and Wastewater  
E - EPA Methods for Chemical Analysis of Water and Wastes



**Figure: Survey Sampling Procedures**

## E. Results

In this section the analytical results before and after pretreatment will be reviewed. Hexavalent chromium results will be compared to the chromium limit (5.0 mg/L) set forth in 40 CFR Part 261.24. Total chromium results include both hexavalent and trivalent chromium content and are for information only. Cyanide results are provided as information to be used for personnel health and safety purposes. Table 2 contains analytical results for each waste drum.

TABLE 2. ANALYTICAL RESULTS

Cyanide, Total Chromium, and Hexavalent Chromium Concentrations (mg/L)

DRUM	$[\text{CN}]_i^-$	$[\text{CN}]_f^-$	Tot $[\text{Cr}]_i$	Tot $[\text{Cr}]_f$	$[\text{Cr}^{+6}]_i$	$[\text{Cr}^{+6}]_f$
1	0.018	-	1135.0	-	1135.0	-
2	0.040	0.018	119.5	966.0	75.0	1420.0
3	5.0	-	103.4	170.7	132.0	<0.05
4	0.068	0.025	124.0	-	124.0	-
5	5.0	<0.005	87.4	170.6	93.0	<0.05
6	10.0	-	109.0	116.0	117.0	<0.05
10	1.625	-	23.9	40.8	11.25	<0.05

### LEGEND:

$[\text{CN}]_i^-$  - initial cyanide concentration (mg/l)  
 $[\text{CN}]_f^-$  - final cyanide concentration (mg/l)  
Tot $[\text{Cr}]_i$  - initial total chromium concentration (mg/l)  
Tot $[\text{Cr}]_f$  - final total chromium concentration (mg/l)  
 $[\text{Cr}^{+6}]_i$  - initial hexavalent chromium concentration (mg/l)  
 $[\text{Cr}^{+6}]_f$  - final hexavalent chromium concentration (mg/l)  
- - sample not taken

## III. CONCLUSIONS

A. Analysis of Drums 1, 2, and 4. Drums 1, 2, and 4 contained chromium trioxide. Pretreatment was attempted on Drum 2, but it could not be accomplished because the pH could not be lowered using sulfuric acid. Since pretreatment was not possible on Drum 2, it was not attempted on Drums 1 or 4. The cyanide concentrations were low (0.018, 0.04, and 0.068 mg/L, respectively). The initial hexavalent chromium concentrations (1135.0, 75.0, and 124.0 mg/L, respectively) exceed the limit (5.0 mg/L). Drum 2 final hexavalent chromium concentration of 1420.0 mg/L exceeds the limit (5.0 mg/L). The final concentration is greater than the initial concentration because the initial sample was taken before the sludge at the bottom of the drum was mixed into solution with the air bubbler.

B. Analysis of Drums 3, 5, 6, and 10. Drums 3, 5, 6, and 10 contain alodine waste. Cyanide removal was performed on Drum 5. The initial cyanide concentration (5.0 mg/L) was low. After cyanide removal, the cyanide

concentration ( $<0.005$  mg/L) was below analytical detection limits. The initial hexavalent chromium concentrations (132.0, 93.0, 117.0 and 11.25 mg/L, respectively) exceed the limit (5.0 mg/L). Pretreatment was performed on each drum. The final hexavalent chromium concentrations ( $<0.05$  mg/L) were below analytical detection limits and do not exceed the limit (5.0 mg/L).

Therefore, the analysis performed on this limited number of drums shows that the process effectively removes cyanide and reduces hexavalent chromium to trivalent chromium.

C. Depending on the quantity of waste generated, the sampling strategy using 10 drums may not be an adequate number of samples to statistically prove that the process works.

#### IV. RECOMMENDATIONS

A. The base should assure that the pretreatment process is fully sanctioned by the Texas Water Commission (TWC). Also the base should develop a waste analysis plan for the pretreatment process which includes the percentage of pretreated drums that should be sampled in order to further verify that the pretreatment process routinely works. The waste analysis plan should be approved by the TWC. According to base personnel, the TWC will approve the pretreatment process upon receipt of analytical results showing that the process does indeed work. The pretreatment process is a rather primitive one; however, it does effectively reduce the hexavalent chromium to trivalent chromium.

B. Cyanide removal should be performed on each drum before chromium reduction. The removal process is simple and eliminates the possibility of the final wastestream containing cyanide.

C. Care should be taken when moving the drums after the pretreatment process. It is possible for the gelatinous metal precipitate to go back into solution, especially if the solution is mixed or allowed to sit for a long period of time. Therefore, the pretreatment process should be performed as close to the point where the wastewater will be discharged to the sanitary sewer as possible. Also, the wastewater should be discharged to the sanitary sewer as soon after pretreatment as possible.

D. The sludge should be sampled and analyzed to determine if it contains any hexavalent chromium. If the sludge contains hexavalent chromium at concentrations above the limit (5.0 mg/L), it should be disposed as hazardous waste. If the hexavalent chromium concentration is below the limit, the sludge can be disposed as municipal waste.

E. Bioenvironmental Engineering should continue to monitor the air for cyanide and chromic acid mist on a routine basis.

F. Pretreatment personnel should always wear faceshields, gloves, and aprons during the process. Extreme caution should be taken when adding chemicals to the drums.

### References

1. Electroplating Wastewater Pollution Control Technology, George C. Cushnie, Jr., Pollution Technology Review No. 115, Noyes Publications, 1985.
2. Samplers and Sampling Procedures for Hazardous Waste Streams, EPA-600/2-80-018, Jan 1980.
3. United States Environmental Protection Agency, "Identification and Listing of Hazardous Waste," 40 CFR 261.

Appendix  
Survey Request Letter

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DEPARTMENT OF THE AIR FORCE  
HEADQUARTERS AIR TRAINING COMMAND (ATC)  
RANDOLPH AIR FORCE BASE TX 78150-5001

2 APR 1990

REPLY TO  
ATTN OF SGPB (7-3764)

SUBJECT Request for On-Site Consultant Services - Randolph AFB

TO USAF OEHL/CC

1. In accordance with the provisions of AFR 161-17, the attached request for consultant services is forwarded for your consideration. The Randolph bioenvironmental engineer is asking for an on-site survey of an experimental hazardous waste treatment procedure.
2. Their request for priority status has been overcome by events. HQ ATC/DEEV has provided the necessary funds to immediately dispose of the 700 drum inventory. Also, chemical paint stripping operations have been replaced at Randolph by bead blasting and once the existing drums of paint stripping wastes are disposed of, no more will be produced.
3. According to ATC/DEEV an alodine pretreatment process (similar to the one at Sheppard) will be instituted at Randolph within a year's time. Until then, the base would still like to proceed with testing their chromium treatment procedure. I believe that base bioenvironmental engineering personnel can conduct the industrial hygiene monitoring portion and I have informed Lt Shaffer of this.
4. The underlying assumption is that in-situ chrome reduction (to below 5 mg/l) of the alodine waste will render the waste non-hazardous and the resulting "process rinse water" can be disposed of through the sanitary sewer system. Recommend that your evaluation include an assessment of the disposal requirements for the final alodine waste stream.
5. I have asked Lt Shaffer to check with both the TAQ and the TWC to determine if the proposed demonstration treatment process requires preapproval or permitting by the State of Texas regulators.
6. Please feel free to contact the Randolph BEE office directly to set up consultant visit dates and to readjust the survey parameters in light of the recent developments.

DAVID A. HADDEN, Colonel, USAF, BSC  
Command Bioenvironmental Engineer  
DCS/Medical Services & Training

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