Final Report

Removing Chromium(VI) from Wastewater by Anion Liquid Ion Exchange (A-LIX)

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LIST OF ACRONYMS

A/E	Aqueous/Extractant (i.e., organic) ratio
AFRL	Air Force Research Laboratory
Alamine® 336	Cognis trade name for their proprietary tri-octyl/decyl amine
Alum, $Al_2(SO_4)_3$	Used for particulate coagulation in Cr (VI) treatment
ALC	Air Logistics Center
A-LIX	Anionic Liquid Ion Exchange
$HCrO_4$ (-I)	Bichromate anion
Conoco® 170 ES	Conoco trade name of kerosene-like organic diluent
Cr	Chromium
Cr $(OH)_3$	Chromium hydroxide
CTL	Columbus Testing Laboratory
E	Extractor
ECAM	Environmental Cost Analysis Methodology
ES	Exempt solvent
ESTCP	Environmental Security Technology Certification Program
Exxal® 10	Exxon trade name for their iso decanol
$FeSO_4$	Ferrous sulfate
$Fe_2(SO_4)_3$,	Ferric sulfate
40CFR	Section 40 of the Code of Federal Regulations
gpd	Gallon per day
GOTW	Government Owned Treatment Works
H_2SO_4	Sulfuric acid
IWTP	Industrial Wastewater Treatment Plant
Kgal/d	Thousand gallons per day
MP&M	Metal Products and Machinery rule by US EPA to reduce allowable Cr and metal discharge levels from metal plating and machining facilities
Na_2CrO_4	Sodium chromate
NFESC	Navy Facilities Engineering Service Center
NaOH	Sodium hydroxide
$Na_2S_2O_5$	Sodium metabisulfite
NPDES	National Pollutant Discharge Elimination System
NPV	Net Present Value
O&M	Operating and maintenance
OSHA/EHS	Occupational Safety and Health Act/Environmental Health and Safety
OO-ALC	Ogden Air Logistics Center
OSU	The Ohio State University
POTW	Publicly Owned Treatment Works
ppm	Parts per million (~ equal to mg/L)
P2	Pollution Prevention
S	Stripper
TSS	Total suspended solids
WAA	Watervliet Army Arsenal
WR	Warner Robins
WR-ALC	Warner Robins Air Logistics Center

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Points of contact can be found in Appendix A.

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1. Introduction

1.1 Background

Chromium (Cr) is widely used within Department of Defense (DoD) and industry for critical metal plating, corrosion control, and surface finishing requirements. However, the hexavalent Cr (Cr (VI) anion is toxic and must be removed from wastewaters prior to discharge. The current technology to remove Cr (Cr (VI) involves Cr (Cr (VI) reduction to Cr (Cr (III) followed by precipitation. While the precipitation process is effective, it generates large amounts of hazardous sludge. These sludges represent the single largest type of hazardous waste at many DoD maintenance facilities. As noted in Table 1-1, based on AF-ALC data, it has been estimated that about 1,960 tons per year of hazardous sludges are generated by the DoD primarily as a result of efforts to curtail Cr (Cr (VI) discharges.[1]

Table 1-1. Chromium Hydroxide Sludge Production

Chromium Hydroxide Sludge Produced from DoD Installations, by Site, ton/year		
Robins AFB (WR-ALC)	Hill AFB (OO-ALC)	DoD Wide (Based on 14 installations)
186	100	1,960

The high cost of handling Cr (Cr (VI) in wastewater and the associated sludge generation is the key reason behind the DoD need to eliminating Cr (Cr (VI) use.[2] While DoD and others are evaluating alternatives to Cr (Cr (VI), it is still the material of choice for corrosion resistance. Until all use of chromium is eliminated, there will be chromium discharges. Therefore, an improved Cr (Cr (VI) removal technology is needed. This project demonstrated the Anionic Liquid Ion Exchange (A-LIX) process for chromium separation and concentration for recycle. A-LIX technology continually extracts the chromate anion, from plating shop wastewater using a water immiscible tertiary amine extractant in a closed-loop process. The chromate anion is later

stripped from the extractant phase of this process and the chromium is concentrated as sodium chromate. The A-LIX process produces a clean water stream that meets chromium discharge requirements, eliminates the need for the reducing agent, and drastically decreases plating shop wastes. A-LIX may also eventually lead to effective water recycle and reuse.

1.2 Official DoD Requirement Statement

1.2.1 Requirements. Chromium (Cr) is widely used within DoD and industry for critical metal plating, corrosion control, and surface finishing requirements. But the hexavalent Cr (VI) anion is toxic, which requires its removal from wastewaters. The federal discharge limits are outlined in 40CFR 433.10 (Metal Finishing). The most stringent limit is 1.71 mg/L (~1.7 ppm) total chrome. The limits at WAA and WR-ALC are 6 ppm total (0.6 ppm Cr (Cr (VI) and 0.3 ppm, respectively. The current technology to remove Cr (Cr (VI) involves precipitation and is moderately effective, but generates excessive amounts of hazardous sludge. These sludges represent the single largest type of hazardous waste at DoD maintenance facilities. As noted below, it has been estimated by Battelle, based on AF-ALC data, that about 1,960 tons per year of hazardous sludges are generated primarily as a result of efforts to curtail Cr (VI) discharges.[1] If instead Army's data are used, then the DoD wide sludge generation rate is estimated to be more than double of this quantity.

The high cost of handling Cr (VI) in wastewater and the associated sludge generation is a key reason behind several DoD ESTRG needs (e.g., 101, 816, and 541 for Air Force) for eliminating Cr (VI) use. While DoD and others are evaluating alternatives to Cr (VI), it is still the choice for corrosion resistance. Until all use of Cr is eliminated, there will be Cr discharges. Therefore, an improved Cr (VI) removal and Army A(2.2.j); and Navy – (2II.1.q). Of particular concern are the proposed Metal Products and Machinery (MP&M) Rule to be applied to DoD facilities that requires much more stringent control of Cr (VI) and other metals [see Navy Need (2.II.1.q)]. This need alone requires the use of a more effective Cr (VI) technology like the proposed anion-liquid ion exchange (A-LIX) technology. Such technologies will eventually lead to effective recycle and reuse of process waters as addressed in the "Tri-Services Wastewater Treatment Strategy."

1.2.2 How Requirements were Addressed. The A-LIX process demonstrated in this program provides a means to effectively control the discharge of Cr from DoD and commercial plating shops. The A-LIX process:

1. Extracts ~ 99% of the Cr (VI) from the wastewater stream providing an effective method to control Cr emissions
2. The process extracts and recovers the Cr in a recyclable form thereby avoiding the production of hazardous Cr sludge
3. The process produces a clean water with Cr (VI) and total Cr levels below existing discharge limits
4. The process requires fewer chemicals and requires less manpower allowing the plating shop wastewater to be treated at a cost lower than conventional precipitation methods
5. The treated water may provide a source of clean water suitable for recycle and/or reuse of the process water.

1.3 Objectives of the Demonstration

The objectives of this project were met. They included the construction of a portable, demonstration-scale device that was operated to validate the previous test results and provide the data needed for a process economics evaluation based on full-scale conditions at the plating shops of the Watervliet Army Arsenal (WAA) located in Albany, NY and the Warner-Robins Air Logistics Center (WR-ALC) located at Robins AFB, GA. The results provide the basis for implementation of the A-LIX process in plating shops and metal treatment operations throughout the DoD.

1.4 Regulatory Issues

The federal discharge limits are outlined in 40CFR 433.10 (Metal Finishing). The most stringent limit is 1.71 mg/L total chrome. Federal environmental regulations, especially the proposed Metal Products and Machinery (MP&M) Rule to be applied to DoD facilities, may require much more stringent control of Cr (VI) and other metals [3, 4]. Compliance with MP&M may require the use of a more effective Cr (VI) technology like the A-LIX technology. Local authorities can institute more stringent requirements. The target Cr (VI) discharge limit was 0.3 ppm, below the federal or local limits on chromium.

Table 1-2. Discharge Regulations

Location	NPDES Limit	
	Daily Weight Limit	Daily Concentration Limit
WR-ALC	1.2 lb average total Cr and 1.7 lb maximum Cr total	0.3 mg/L (ppm) average total Cr and 0.45 mg/L maximum
Watervliet Army Arsenal	3 lb total Cr and 0.3 lb Cr (VI)	~6 mg/L total Cr and ~0.6 mg/L Cr (VI) [a]

(a) Conversion to ppm based on 58,000 gallons per day of Cr contaminated effluent

The oil and grease levels are also regulated. The WR-ALC demonstrated level of 5 ppm is well below the 15-ppm limit at WR-ALC.

1.5 Previous Testing of the Technology

A-LIX tests were conducted at WR-ALC at Robins AFB, GA, with plating shop wastewater in 1997 [5]. These tests provide valuable feasibility data for reducing the Cr (VI) concentration in the aqueous stream from 2 – 10 ppm to less than 0.05 ppm. Operating experience and limited parametric testing focused on pH control, stabilized operation, and throughput that met the technical performance requirements and economic benefits. Cr (VI) concentration increased in the stripping solution to 1400-ppm over 20 days of cumulative testing. Eventually the concentration would rise sufficiently to make a valuable byproduct. To test the A-LIX operation under this condition, sodium chromate was added to the strip mixer/settler to raise the Cr (VI) concentration to 20,000 ppm. The Cr (VI) level in the clean water was consistently reduced to well below 0.05 ppm. Discussions with a chemical recycler indicated that a 20,000-ppm Cr concentrate would be a viable source for Cr recycling.

1.6 Demonstration Results

The technical and economic goals and the program achievements are noted below.

Goals	Accomplishments
Reduce the Cr (VI) concentration in the aqueous stream below a target level of 0.3 ppm	A Cr (VI) extraction efficiency of 99+% was demonstrated. This allowed the production of a $\leq$ 0.3 ppm Cr (VI) level in the product water under normal operating conditions. However, at extremely high feed Cr (VI) conditions, while the extraction level remained near 99%, the 0.3 ppm Cr (VI) could not always be met.
Produce a useful concentrate using the compact, automated A-LIX plant	This was achieved and the concentrate was successfully recycled at the Inmetco plant in Pennsylvania
Demonstrate significant cost savings and equipment payback in 3 years or less	The payback periods for the two sites evaluated were 3.9 and 2.4 years for WAA and WR-ALC, respectively. Treatment costs per 1,000 gallons wastewater were $17.50 and $19.90 for WAA and WR-ALC, respectively.

The A-LIX demonstration at WR-ALC removed oil and grease levels to 5 ppm, which was well below the 15-ppm limit at WR-ALC.

2. Technology Description

2.1 Description

2.1.1 Technology Development and Application. The use of A-LIX is a novel extension of liquid-liquid extraction processes common to the chemical and metallurgical industries. Ion pairing is the primary extraction mechanism that selectively removes the Cr (VI) anion from dilute aqueous solution into an oil soluble extractant. The extractant is a tertiary amine (R_3N). In order for the amine to extract the bichromate anion, $HCrO_4$(-I), the extractant must first be protonated by the addition of an acid. In our process, this is accomplished by the addition of sulfuric acid (H_2SO_4). After the Cr (VI) is extracted, it must be stripped. This is accomplished by contacting with base, i.e., sodium hydroxide (NaOH). The reaction simultaneously regenerates the extractant and transfers the Cr to the aqueous phase for recovery. The addition of small amounts of water keeps the water "in and out" flows in balance and provides a way to purge the Cr concentrate from the system. The program demonstrated that a commercially available amine extractant, Alamine® 336, is an effective extractant when used as 5-percent solution in high flash-point organic[5]. Figure 2-1 illustrates the test conditions and performance of the 2-extraction-stage mixer/settler system tested at WR-ALC. A flow rate of 10,000 gal/day (gpd) of dilute Cr (VI) wastewater (from rinse tanks and other plating shop operations) was continuously contacted in countercurrent flow with the extractant to remove Cr (VI) from the aqueous effluent to produce effluent with discharge concentrations below 0.6 ppm composed of 0.2 ppm Cr (VI) and 0.4 ppm Cr (III). The Cr (VI) was then concentrated to 11,000-ppm (1.1 percent), representing a viable chromium source for chemical suppliers to reuse. Tests showed that other metals are not extracted to any significant extent in the A-LIX process, because the

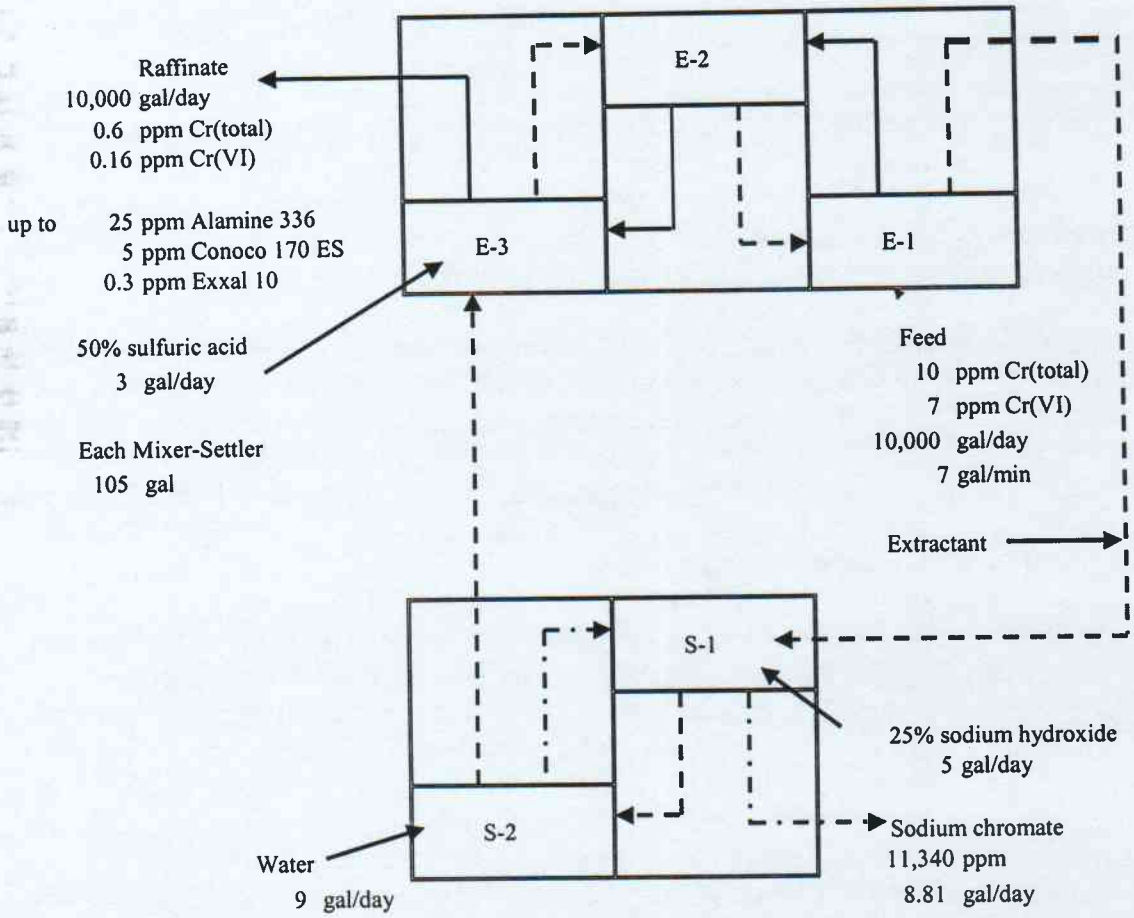


Figure 2-1. Demonstration Test Conditions and Results from WR-ALC Tests

positively charged extractant only extracts anions; the other metals found in plating shop effluent are found in the cation (i.e., positively charged) form.

A material balance on Cr (total) indicates 0.88 lb Cr/day enters with the feed. The raffinate and Cr concentrate contain 0.05 and 0.83 lb Cr (total)/day, respectively. Thus, the A-LIX process was essentially in balance.

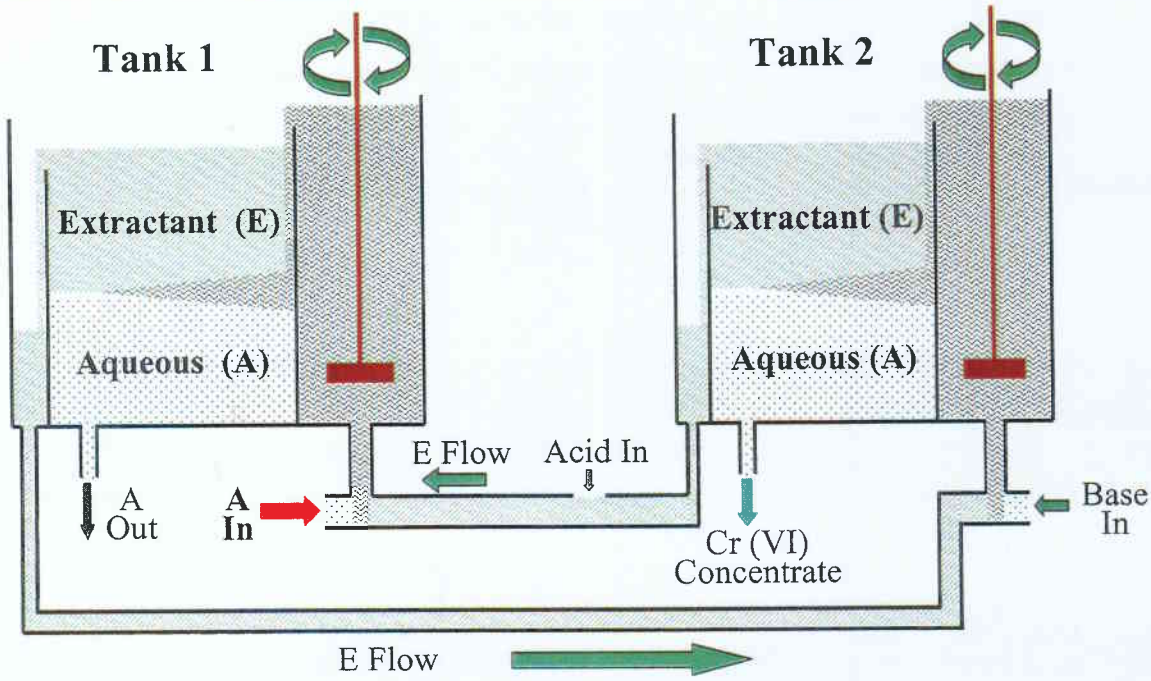
Materials of construction were evaluated to assess their compatibility with the acid and base as well as the extractant components. The Alamine® 336 extract, Conoco® 170 ES carrier fluid, and Exxal® 10 (iso decanol) modifier were all found compatible with the polyvinyl chloride used in the mixer/settlers, polyethylene used in auxiliary tank, and pumps. It was found to have poor compatibility with rubber (used in the seals of some of the pumps).

2.1.2 Process Description. The A-LIX process is shown schematically in Figure 2-2. The aqueous rinse water from the plating shop contains many metals. Cr (VI) is present mostly as the bichromate anion, $HCrO_4$ (-I). The A-LIX system employs a series of mixer/settlers to achieve a liquid-liquid extraction of the Cr. The Cr-contaminated feed water is introduced into the bottom of the first mixer where it is contacted with hydrogen ions, H(+), in the form of sulfuric acid, and a tertiary amine (R_3N) extractant. Ion pairing results in capture of the Cr (VI) as part of an oil soluble salt ($R_3NH^+HCrO_4^-$) in the extractant phase.

The high interfacial surface area provides fast kinetics even with feed Cr (VI) levels as low as 1 ppm. The extractant and cleaned water overflow the mixer into a settler. The Cr-extracted aqueous phase is drawn off the bottom of the settler. The low-density extractant separates from the aqueous phase in the settler and floats to the surface of the settler where it is drawn off and sent to the mixer in the stripper section. In the stripper, NaOH is added to react with the salt to regenerate the extractant and release the captured chromate as sodium chromate (Na_2CrO_4). The stripped extractant and Cr concentrate overflow the mixer into the settler. The Cr (VI)-free extractant floats to the surface of the settler, is withdrawn, and is recycled back to the extraction mixer/settler. This continuous regeneration keeps working capital low. The aqueous Cr concentrate is withdrawn from the bottom of the stripper settling-chamber for recycle.

The extractant used in this process is Alamine® 336. It has been found to be a selective extractant for Cr (VI), even over sulfate ion. Exxal® 10 is added as a modifier to decrease phase separation time and increase the ion-pairing kinetics. To minimize costs and control performance, only a small portion of the extractant phase is actually the amine or the modifier. The majority is an organic diluent. The extractant phase used in these tests was composed of 5 vol. % Alamine® 336 (Cognis), 5 vol. % Exxal® 10 [isodecanol (Exxon Chemical, Corp.)], and 90 vol. % Conoco® 170 ES aliphatic diluent (Conoco, Inc.).

A-LIX Process



$R_3N + H^+ + HCrO_4^- \longrightarrow R_3NH^+HCrO_4^-$ $\quad$ $R_3NH^+HCrO_4^- + 2NaOH \longrightarrow 2H_2O + Na_2CrO_4 + R_3N$

Figure 2-2. A-LIX Process Schematic

2.2 Strengths, Advantages, and Weaknesses

The demonstration involved treatment of simulated rinse water from the WAA plating shop and wastewater from the WR-ALC plating shop. The A-LIX process worked equally well in both applications. The A-LIX process could also be used for the treatment of general wastewater that is contaminated with Cr. It appears that as long as the Cr content was in the form of Cr (VI), reasonably high in Cr (at least a few ppm), and the wastewater can be acidified to the appropriate pH level (~ 3) the process should extract Cr. Excess particulates would eventually foul the system, so it will be necessary to screen the influent to remove solids. The presence of other metals should not have a detrimental affect. Oils in the water would likely be extracted into the extraction phase with little detrimental affect.

Alamine® 336 must be protonated with an acid to extract metal anions. Even in a high pH environment with high levels of lead or aluminum, the wastewater could be acidified and successfully processed for the extraction of Cr. However, high cyanide (CN) containing streams should not be treated. The acidification of the CN wastewater could result in the release of toxic hydrogen cyanide gas. If the CN wastewater was oxidized for CN destruction, the effluent could then be treated by A-LIX for Cr extraction and recovery. However, the presence of residual oxidants might result in the degradation of the extractant and reduce extractant life.

Table 2-1 presents a comparison with other Cr (VI) control techniques.

Table 2-1. Comparison of A-LIX and Alternative Treatment Technologies

Technology	Pollution Prevention or Compliance	Hazardous Waste	Ionic Selectivity	Capital/ Operating Cost	Other Benefits/Issues
A-LIX	Both	No	Yes	Medium/ Low	Multiple applications Non-proprietary commercial basis
$SO_2/H_2SO_4/$ NaOH (current OO-ALC)	Compliance	Yes	No	Medium/High	Discharge limit 0.2 ppm Need sludge conditioning
$FeSO_4$/NaOH (Procedure use before June 2001 at WR-ALC)	Compliance	Yes	No	Low/High	Discharge limit 0.2 ppm Need sludge conditioning
Reverse osmosis (demonstrated)	Both	No	No	High/High	Good for water reuse
Ion exchange	Compliance	Yes	No	Medium/ Unknown	Not good for Cr (VI) recovery
Superlig (Kathy Ford testing)	Both	No	Yes	Medium/ Unknown	Proprietary
Diffusion dialysis (Nick Stercel)	Both	No	Limited	High/ Medium	Limited to conc. acid recovery
Selective distillation (Phil Darcy)	Both	Yes	Limited	High/ Medium	Limited to conc. acid recovery

One related ongoing ESTCP program uses molecular recognition technology and is being tested by Dr. Katherine Ford of Naval Facilities Engineering Services Center.

A-LIX advantages include:

- No production of hazardous wastes
- Selectivity for the specific ion of interest
- Moderate capital and low operating costs

- Suitable for multiple-site applications
- Non-proprietary technology
- Based on well-establish commercial liquid-liquid extraction technology
- Is not labor intensive.

A-LIX weaknesses include:

- The A-LIX process does not provide a complete solution to plating-shop wastewater treatment. A secondary caustic addition and metals precipitation, settling, and dewatering step is needed to remove cationic metals such as copper, cadmium, lead, etc.
- The recovered Cr cannot be used directly in the plating operations
- The recovered Cr can be recycled into the metals industry, but at a charge of ~$1/gal in large quantities
- The recovered Cr must be transported to Pennsylvania for recycle. This is a weakness due to the charges for transportation and liability issues due to potential spills
- The basis for estimation of full-scale A-LIX plant was based on escalating the design, procurement, equipment, and installation costs for the 10,000 gpd land/sea box demonstration unit. Better data for significantly larger plants are needed.

2.3 Factors Affecting Cost and Performance

The following factors influence the cost and performance of the A-LIX process and its advantage over alternative conventional Cr (VI) treatment technologies:

- Method of conventional Cr (VI) treatment
- Concentration of Cr (VI) and Cr (III) in the wastewater
- Cost for sludge disposal generated by conventional Cr (VI) treatment
- Degree of Cr concentration (a limit of 20,000 to 40,000 ppm is required to prevent sodium chromate precipitation)
- Fee for Cr concentrate recycling and transportation distance from the plant site to the Inmetco recycling facility in Ellwood City, PA
- pH required for conventional Cr (VI) treatment and for the A-LIX extraction step
- Required A-LIX mixer and settler residence times
- Extractant composition
- Wastewater temperature (due to impact on extractant loss rate and precipitation of Cr concentrate in the stripping circuit)
- Extractant, especially Alamine® 336, loss rate.

3. Site/Facility Description

3.1 Background

The WAA and WR-ALC test sites were selected based on the following:

1. Need to control Cr (VI) discharge from large plating shop operations
2. Large wastewater production
3. High concentrations of Cr (VI) wastewater
4. Interest in exploring innovative solutions
5. Space available to accommodate the portable system.

3.2 Site/Facility Characteristics

The two selected test sites operate large plating shop operations. Each is described in general terms in the following sections.

3.2.1 Watervliet Army Arsenal. The WAA is a Munitions and Armaments Command Installation of Operations Support Command (Provisional) under the U. S. Army Materiel Command. It was founded in 1813 to support the "Second War for Independence," the War of 1812; the arsenal has been a valuable resource ever since. Located along the Hudson River, just a few miles north of the state capital at Albany, NY, WAA continues to produce today's high tech, high-powered weaponry. Cannon -- the finest cannon manufactured in the world today -- remains the principle product of Watervliet Arsenal. The guns manufactured at Watervliet Arsenal provide the firepower for the Army's main battlefield tank, the M1A1 Abrams.

The co-location of WAA and Benet Labs allows for complete lifecycle management from ideas through research and engineering, into prototyping and testing, and finally, into full-scale production all at one site. This offers unique possibilities for timely creativity and production.

A 10-year $350-million renovation program completed in 1992 has made Watervliet Arsenal one of the most sophisticated, automated heavy manufacturing and machining centers to be found anywhere -- private or public sector.

The WAA contains one of the largest plating shops in the DoD. The plating/surface coating facilities are available to handle small parts as well as long cylindrical parts up to 30-inches diameter x 33-feet long.

The wastewater is divided into a soluble-oil contaminated and regular Cr-contaminated wastewater. Average data on the Cr-contaminated wastewater and the method of wastewater treatment is noted in Table 3-1.

Prior to actual experimental testing, it was discovered that the activity level of the WAA plating shop had dropped dramatically. Rather than plating many gun barrels per month, demand had dropped to a smaller number. Therefore, there would not be sufficient plating shop rinse water to support the demonstration program. It was suggested by WAA that a drum of the actual plating solution be supplied and this could be diluted with water to simulate plating shop rinse water. Since the dilution could be done as well in Columbus as in Albany, NY, it was decided to do the WAA demonstration testing at Battelle in Columbus, OH. This change in the experimental testing site was approved by ESTCP prior to initiation of testing.

Table 3-1. WAA and WR-ALC Test Site Characteristics

Parameter	WAA	WR-ALC
Common Values		
Flow rate	58,000 gpd	69,000 gpd
Cr (VI) inlet, average	25 ppm	10 ppm
Inlet wastewater pH	7	~6
Cr (VI) Reduction and Metals Precipitation		
Acidifying agent	H_2SO_4	None (recently switched to H_2SO_4)
Cr (VI) reductant	SO_2	Sodium meta bisulfite (recently switched to sodium bisulfite)
Metal hydroxide precipitation agent	NaOH	NaOH
Flocculating agent	Polymer	Polymer
Coagulation	Alum	Ferric sulfate (recently reduced)
Sludge Handling		
Metal sludge dewatering technique	Drying beds	Plate and frame pressure filtration

3.2.2 Battelle. The Battelle Memorial Institute (Battelle) is located in Columbus, OH north of the downtown and adjacent to the Ohio State University (OSU). The main Battelle campus consists of 19 buildings bordered on the west by the Olentangy River and OSU on the north. The A-LIX demonstration land/sea box was installed inside Building 9. This two-story building houses the Battelle machine shop and many industrial test and development areas. Battelle's Building 9, the location of the demonstration land/sea box, is displayed in Figure 3-1.

3.2.3 WR-ALC. The WR-ALC is located in Warner Robins, GA at Robins AFB. Robins Air Force Base is the largest industrial complex in Georgia. It has over 14 million total square feet of facilities situated on 8,722 acres. It employs more than 19,800 men and women (4,967 military members, 12,554 civilians, 2,327 contractors) [(6)]. The effluent from the plating shop, Building 142, is directed to the industrial wastewater treatment plant (IWTP) No. 2. The plant has been modified several times, but during the demonstration period was operated on a manual, batch-wise operation. The influent rates to and effluent flow rates from the IWTP are monitored on an infrequent basis. Average data were noted in Table 3-1. At WR-ALC, the effluent from the plating shop, Building 142, is directed to IWTP #2 [(7)]. Aerial photographs of Robins AFB showing the location of the plating shop, the IWTP, and the location of the A-LIX unit are shown in Figures 3-2 and 3-3.

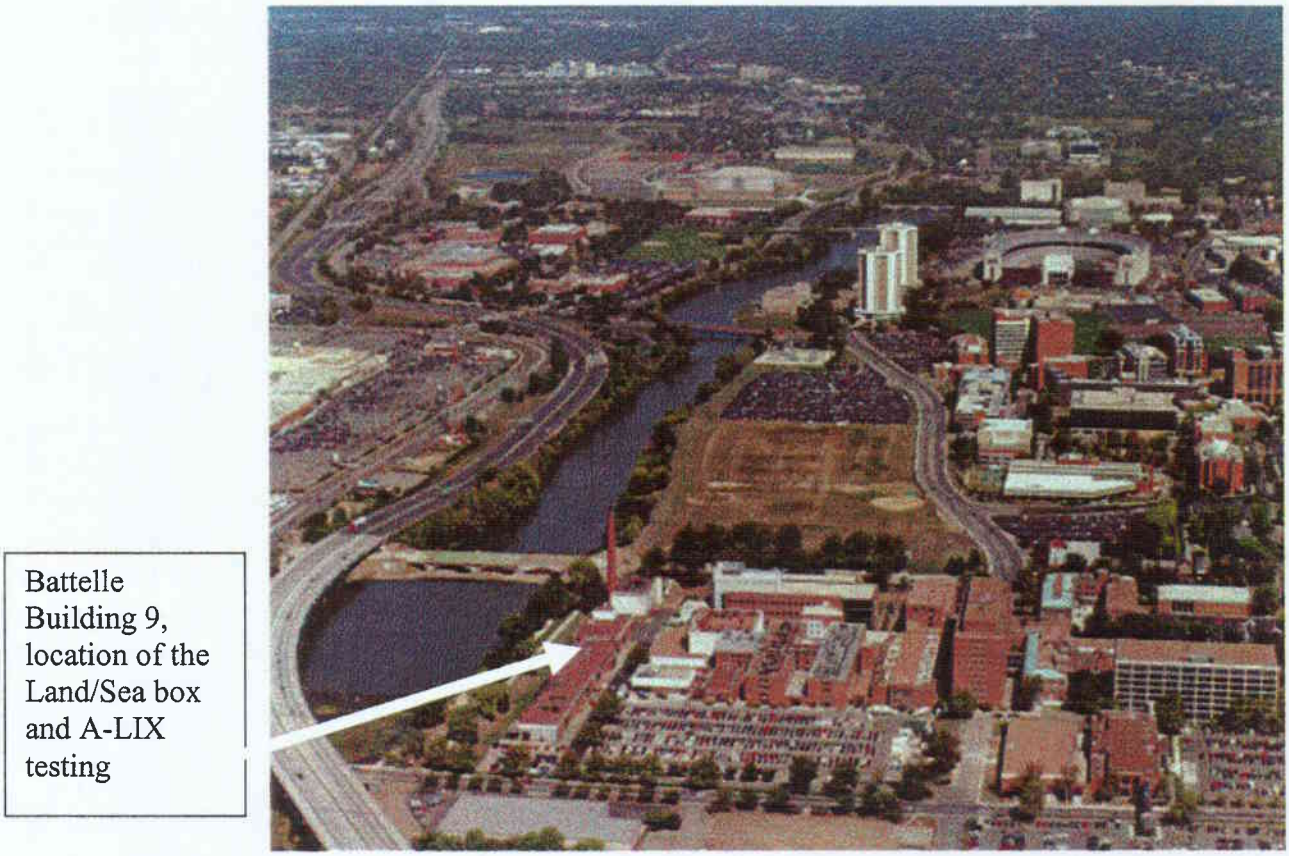
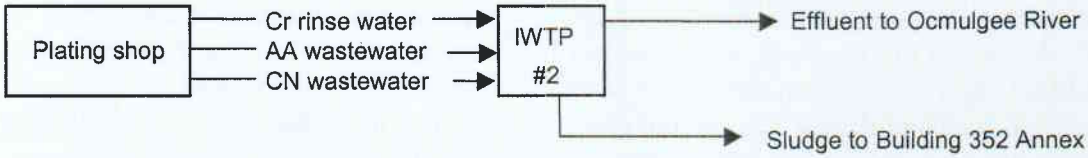
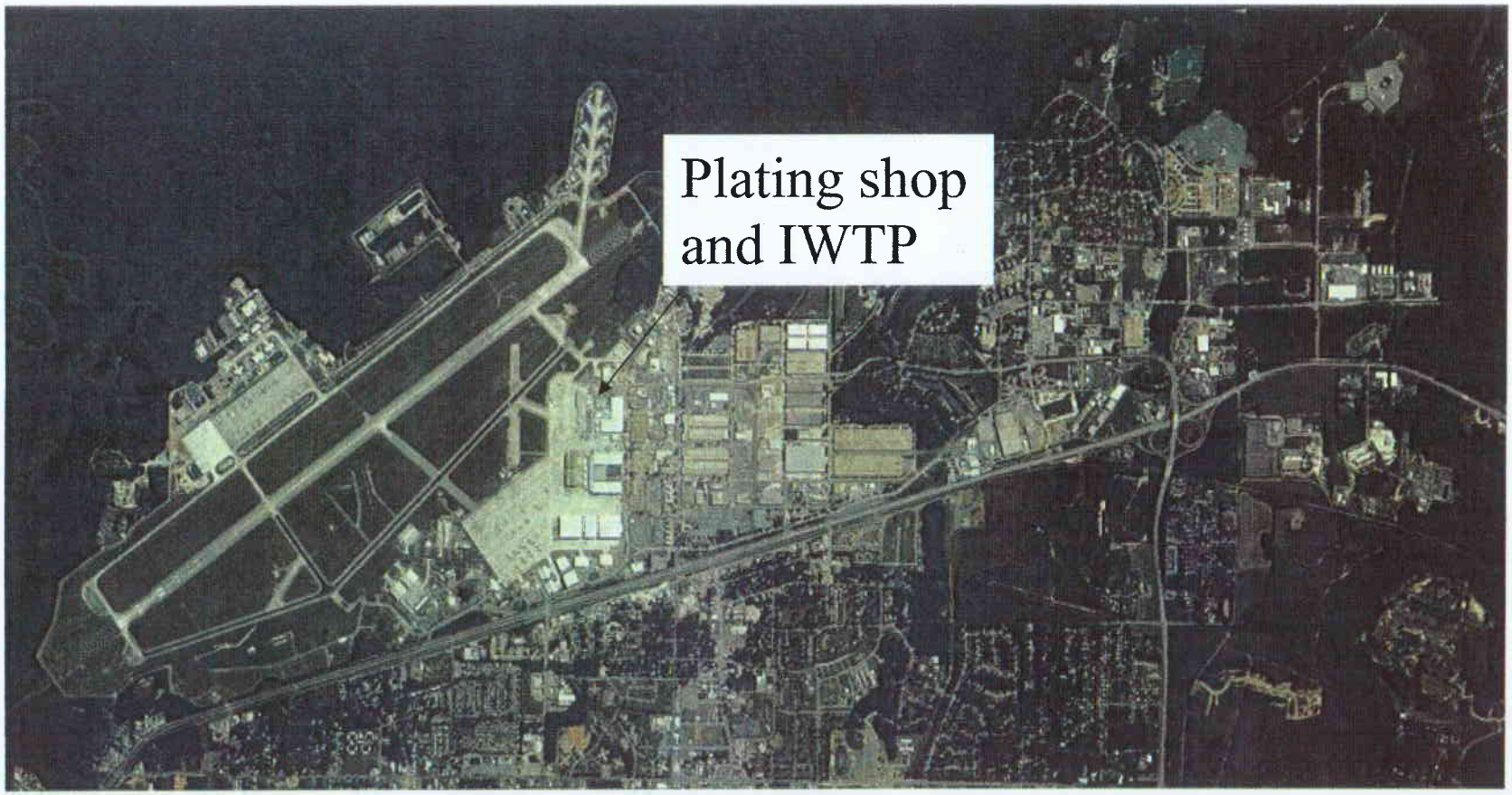


Figure 3-1. Aerial Photograph of the Location of the A-LIX Unit at Battelle

As noted below, there are three lines extending from sumps in the basement of the plating shop.



The influent consists of chrome plating rinse water, acid alkali (AA) wastewater, and cyanide (CN) plating rinse water. Very little CN wastewater is generated. The effluent rate is similar to the influent rate except for the small quantity of water discharged with the dewatered sludge. The influent rates to and effluent rates from the IWTP #2 are monitored on a regular basis. In CY 1999 the clarified water flow rate from the IWTP #2 ranged from a minimum of 15,000 gallons/day (Kgal/d) to a maximum of 135 Kgal/d; the average was 69 Kgal/d.



ROBINS AFB, WARNER ROBINS, GA 1996

Figure 3-2. Aerial Photograph Showing the Plating Shop and IWTP at Robins AFB

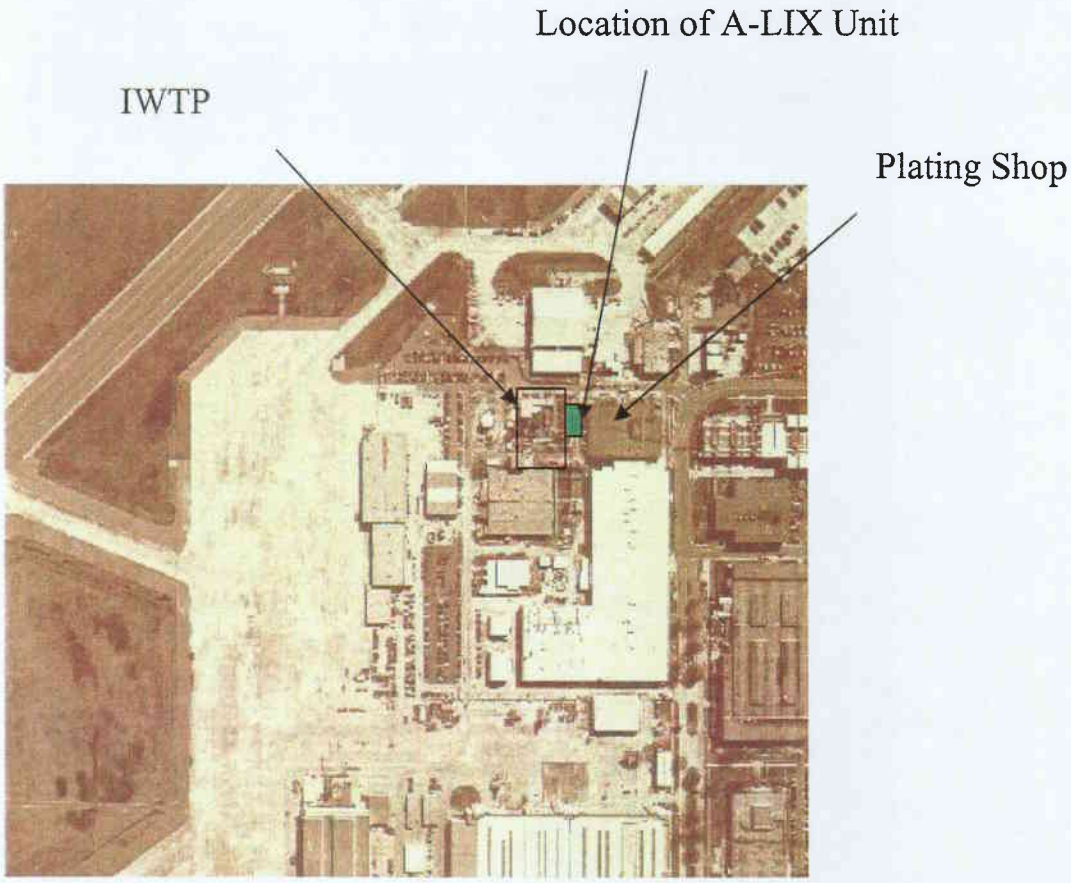


Figure 3-3. Aerial Photograph of the A-LIX Unit at Robins AFB

The A-LIX equipment was configured into a 40-ft long by 8-ft wide by 8-ft high land/sea box. The box was located behind a secondary containment berm within which a 1500-gal tank was located to hold the clean product water. Both the secondary containment berm and the land/sea box were located along the fence surrounding the IWTP and between the plating shop and the IWTP #2.

IWTP #2 was designed to handle up to 365 ppm of Cr (VI). The plant has been modified several times, but now is operated on a manual, batch-wise operation. No automated controls are used to meter in chemicals.

For many years, the base used ferrous sulfate ($FeSO_4$) for Cr (VI) reduction. Within the last couple of years, they have switch to sodium meta bisulfite ($Na_2S_2O_5$) powder. After reduction, the pH of the suspension is raised by the addition of NaOH. Ferric sulfate,

$Fe_2(SO_4)_3$, in acid is added as a floc conditioner and an organic polymer is added to promote solids removal. The suspension of precipitated solids is pumped to a clarifier. The underflow is pumped to a thickener, and the solids are ultimately dewatered in a filter. The solids are loaded in 1-ton containers and recycled for their iron content. In late June 2001, after completing the A-LIX tests, the bases switched to a sulfuric acid/liquid sodium bisulfite system for Cr (VI) reduction.

More details on the operation of the IWTPs at WAA and WR-ALC are found in the Demonstration/Validation Plan [6] Cost and Performance Report [8].

4. Demonstration Approach

4.1 Performance Objectives

The performance objectives are noted in Table 4-1. Quantitative criterion 1, 2, and 3 and qualitative criterion 1 were met. The economic analysis indicated the payback for a full scale A-LIX unit ranged from 2.4 to 3.9 years; the average is slightly more than 3 years.

Table 4-1. Performance Objectives

Type of Performance Objective	Primary Performance Criteria	Expected Performance Metric
Quantitative	1. Validate capacity	10,000 gpd
	2. Validate raffinate (i.e., clean water) Cr (VI) and oil levels	<0.3 ppm Cr (VI) and <50 ppm oil in product water <5 ppm Alamine® 336 in the product water
	3. Increase Cr (VI) concentrate	>20,000 ppm
	4. Validate process economics	<3-year payback for full scale
Qualitative	1. Reliability	Demonstrate robust operation with varying feed quality

4.2 Physical Setup and Operation

4.2.1 Demonstration Set-Up and Start-Up. The portable A-LIX plant was constructed off-site over a three-month period. Shakedown of the plant was conducted in January and February 2001 at Battelle in Columbus, Ohio. Testing with the WAA material was conducted in March and April 2001. The A-LIX plant was located in a 40-ft long x 8-ft wide x 8-ft high land/sea box. The equipment configuration is shown in Figure 4-1.

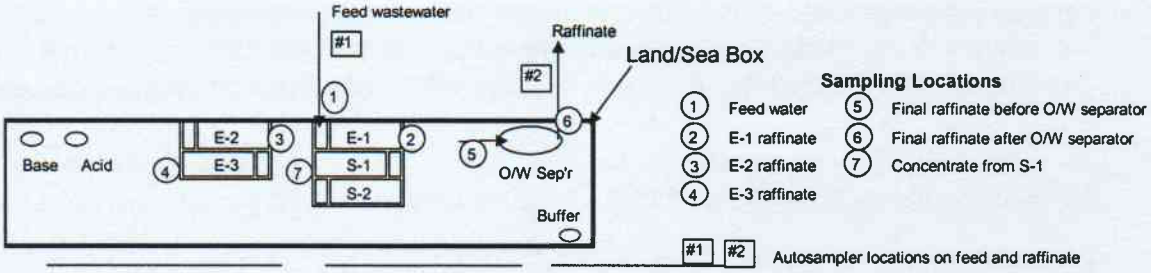


Figure 4-1. Configuration of Equipment in the Land/Sea Box

Tap water and Cr plating batch solution were mixed and pumped into a 1500-gal feed tank to make a consistent feed to the A-LIX unit. The product water (referred to as the raffinate) was sent to a 500-gal collection tank and then to the Battelle drain. Both feed and raffinate were monitored for pH and Cr (VI).

The land/sea box holding the A-LIX equipment was moved to the WR-ALC site in early May 2001. Testing was conducted in May and June 2001. Raffinate and concentrate tanks were located in an adjacent secondary containment tarp. Both were located along the fence line next to the IWTP. The base provided electrical power and tap water. The feed wastewater was withdrawn from a receiving basin in IWTP No. 2. It was pumped through a filter and into the land/sea box for processing. The raffinate was discharged to the IWTP where the water was neutralized and all metals precipitated prior to thickening and filtration.

4.2.2 Period of Operation. The test periods are noted in the following table.

Operation	Dates
Shakedown at Battelle	January – February 2001
WAA material testing at Battelle	March – April 2001
WR-ALC testing at Robins AFB	May - June 2001

4.2.3 Amount/Treatment Rate of Material Treated. The plant was designed to continuously process ~ 7 gpm (10,000 gpd) of Cr (VI) rinse water. Testing at Battelle and WR-ALC were a mixture of 12 to 24 hr/day runs. Approximately 300,000 gal of simulated plating shop rinse water was treated at Battelle and ~150,000 gal were treated at the WR-ALC test site.

4.2.4 Residuals Handling. Four types of residuals were produced during testing. The residuals were handled as noted below:

- Filters: an in-line cartridge filter was located on the process feed stream entering the A-LIX system. The filters were used to remove solids from the feed stream greater than approximately 10 microns. Because Cr (VI) is highly soluble, only the water entrained in the filter cartridge at the time of its disposal contained measurable amounts of Cr (VI). These cartridges were disposed of as hazardous wastes.

- Extractant: the extractant used for collecting the Cr (VI) was stripped at the conclusion of the demonstration test program at Battelle and WR-ALC. It was transferred to 55-gal drums and shipped with the demonstration plant to the demonstration site or is in a storage location at Battelle.
- Cr concentrate: at Battelle all the concentrated Cr (VI) water, containing ~20,000 ppm of sodium chromate (Na_2CrO_4) were collected. About six 55-gal drums of concentrate were shipped to Inmetco for recycle evaluation. At WR-ALC, the majority was bled back into the IWTP for treatment; a small sample was saved for analysis.
- Rag layer: the waste rag layer containing water, extractant, Cr (VI) and Cr (III) in the form of green chromic hydroxide, $Cr(OH)_3$ particles separated at the end of the series of runs was collected and sent to Inmetco for disposal.

4.2.5 Operating Parameters for the Technology. The key operating parameters for the A-LIX plant were the residence times in the mixers and settlers, the extraction A/E ratio (volume ratio of aqueous phase to extractant phase in the settlers), and the pH of the extraction and stripping stages. Automated pH controllers were used to monitor and automatically control the addition of acid and base to the plant.

4.2.6 Experimental Design. A series of 8 experiments described in Table 4-2 were conducted to address the critical technical issues including operability and reliability, control, extractant losses, concentrate value, and life cycle cost.

Table 4-2. A-LIX Experimental Design Matrix for the WAA Tests

Test Number	Conditions
Run No. W-1	Center Point; mixer residence time = 2 min., settler residence time = 8 min., A/E= 6/1, extraction pH = 3.5, strip pH = 11, baseline impeller rpms
Run No. W-2	Mixer residence time = 2 min., A/E = 6/1, 110% of baseline impeller rpms
Run No. W-3	Mixer residence time = 2 min., A/E = 6/1, Either 120% or 90% of baseline impeller rpms
Run No. W-4	Mixer residence time = 2 min., A/E = 8/1, new baseline impeller rpms
Run No. W-5	Mixer residence time = 2 min., A/E = 10, new baseline impeller rpms
Run No. W-6	Mixer residence time = 2 min., best A/E and impeller rpms from Run Nos. 1 through 5
Run No. W-7	Mixer residence time = 2 min., new baseline A/E and impeller rpms, Spike Strip No. 1 to ~20,000-ppm Cr (VI), withdraw concentrate to maintain Cr (VI) at ~20,000-ppm
Run No. W-8	Mixer residence time = 1 min., A/E = 1/6, new baseline impeller rpms, withdraw concentrate to maintain Cr (VI) at ~20,000-ppm

Run No. W-1 was the primary start-up run for the system. The run was considered complete when steady operation was achieved and maintained for one hour. Such operation was defined by: constant feed, raffinate, and extractant flow rates; constant Cr (VI) concentrations in the feed and raffinate; and constant interface levels in the settlers. The liquid levels and pH of the extraction and stripping stages were pre-set based on

startup tests conducted prior to the Run Nos. W-1 through W-8 program. Run Nos. W-2 through W-5 are modifications to Run No. W-1 to help optimize system performance. Only one parameter was altered at a time. After three hours of operation, settings were changed to a new set of conditions.

Run No. W-6 took place using the optimized conditions found from the previous runs. The duration of the WAA run was ~1 week to demonstrate reliable system performance. During this run, the concentration of Cr (VI) in the first stripping unit increased to ~1,000-ppm. For Run No. W-7, enough chromic acid (CrO_3) and sodium hydroxide (NaOH) were added to the first stripping unit to increase the aqueous concentration to approximately 20,000 ppm while maintaining the pH near 13. During continuous operation, water was pumped into stripper No. 2 which caused concentrate to flow to Stripper No. 1, which caused concentrated strip solution to overflow into a holding tank. The water addition rate was calculated to maintain the Cr (VI) concentration at this elevated level. This test confirmed that steady operation was possible while simultaneously producing the Cr (VI) concentrate and the <0.3-ppm Cr (VI) raffinate.

Run No. W-7 was conducted over a period of 20 days. It demonstrated robustness and the ability to produce a consistent raffinate and Cr concentrate.

Run No. W-8 was designed to evaluate the system at twice the throughput of the previous runs. The feed rate for this run was intended to be 20,000 gpd; however, due to plumbing and pumping limitations, a rate only slightly greater than the nominal 10,000-gpd rate could be achieved and the run was terminated.

A similar set of runs was not needed since the information needed to set the device was available from the WAA test. The first WR-ALC run (designated R-1) corresponded to Run No. W-6 in Table 4-2. And the second WR-ALC test (R-2) corresponded to Run No. W-7.

4.3 Sampling/Monitoring Procedures

For the short-term experiments, Run Nos. W-1 through W-5, raffinate and concentrate samples were taken at frequent intervals to confirm steady-state operation. Sample ports with a discharge pipe and valve were installed where feasible. Grab samples were taken at the following locations (see Figure 4-1 presented earlier for sample locations):

1. Feed (by sample port)
2. Product water after each extraction stage (by syringe inserted into the overflow weir)
3. Raffinate, before the oil/water (O/W) separator (by sample port)
4. Raffinate (after the O/W separator) (by syringe inserted into the overflow sump)
5. Concentrate (by syringe inserted into the overflow weir).

Two auto samplers were used in experiments Nos. W-6 (R-1) and W-7 (R-2) (the long duration, steady-state tests). One was used to collect a 24-hour composite sample of the feed (No. 1 in Figure 4-1) and the second auto sampler was used to collect a composite of

the final raffinate (No. 2 in Figure 4-1). Samples for oil and grease determination were collected in 1-L glass bottles with Teflon seals; the samples will be acidified with sulfuric acid to a pH of <2, and stored in a refrigerator at 4 C until analyzed. Samples collected for total RCRA metals were acidified with 5 mL nitric acid/L of sample and stored in plastic bottles. The grab samples as well as samples from the auto-sampler were stored in a refrigerator until analyzed by Columbus Testing Laboratories or the WR-ALC analytical lab at the IWTP.

4.4 Analytical Procedures

The following analytical procedures were followed:

- pH: The pH of the solutions was determined using a hand held pH meter calibrated weekly with standard solutions.
- Cr (VI) in the raffinate: The Hach diphenylcarbazide colorimetric method was used for all Cr (VI) analyses. This method allowed Cr (VI) concentrations from 0.01 to 0.50 ppm to be determined. The detection limit was 0.1 ppm. The method is US EPA accepted for analysis of wastewater.
- Metals in the raffinate and concentrate: Total metal analyses were determined by Atomic Absorption techniques.
- O/G: Oil and grease determinations were made following gravimetric methods (US EPA Method 413.1).
- Alamine® 336 in raffinate was determined by a method suggested by the extractant vendor.

Columbus Testing Laboratory was used for O/G, Alamine® 336, and total metals determinations for experiments conducted at Battelle. For tests at WR-ALC, the on-site base analytical laboratories were used for total metals analyses, whiles samples for O/G and Alamine® 336 content were again sent to Columbus Testing Laboratory.

Preparation requirements and detection limits are noted in Table 4-3.

Table 4-3. Summary of Analytical/Testing Methods

Parameter	Method	Detection Limit, ppm	Preservative	Maximum Holding Period	Container Type G= Glass P = Plastic and Sample Size
pH	EPA 150.1	0.1	None, conducted in situ	NA, analyze immediately	NA 50 mL
Cr (VI)	Spectrophotometric, Hach, diphenyl-carbazide colorimetric method, APHA Std Methods, 13th ed., 158 (1071)	0.01	None, conducted immediately	NA	NA 10 mL
Total metals	Atomic absorption SW-846-7140	0.01	5 mL HNO_3/L	6 months	P 100 mL
Oil and grease	Spectrophotometric US EPA 413.2	1	2 mL H_2SO_4/L	24 days	G 1 L
Alamine® 336 in raffinate	Henkel, "The Colorimetric Determination of Alamine® 336 in Solvent Extraction Raffinates and Pulps."	1	None	Not available	Sample containing ~ 0.002 g of Alamine® 336

5. Performance Assessment

5.1 Performance Data

5.1.1 Watervliet Army Arsenal Performance Data. The commercial-scale testing using WAA depot feed processed about 300,000 gallons (4.2 million liters) of feed during the seven runs with the following results.

Run Nos. W-1 – W-5: This series of runs established the primary operating conditions; feed rate; E/A flow ratio; stirrer tip speeds; and pH control.

Run No. W-6: This run demonstrated operability and extraction performance over a 5 day 24 hr/day test. As noted in Figure 5-1, excellent Cr (VI) removal was achieved even

with variable levels in the Cr (VI) feed water (6-16 ppm). Table 5-1 provides the specific run parameters and results.

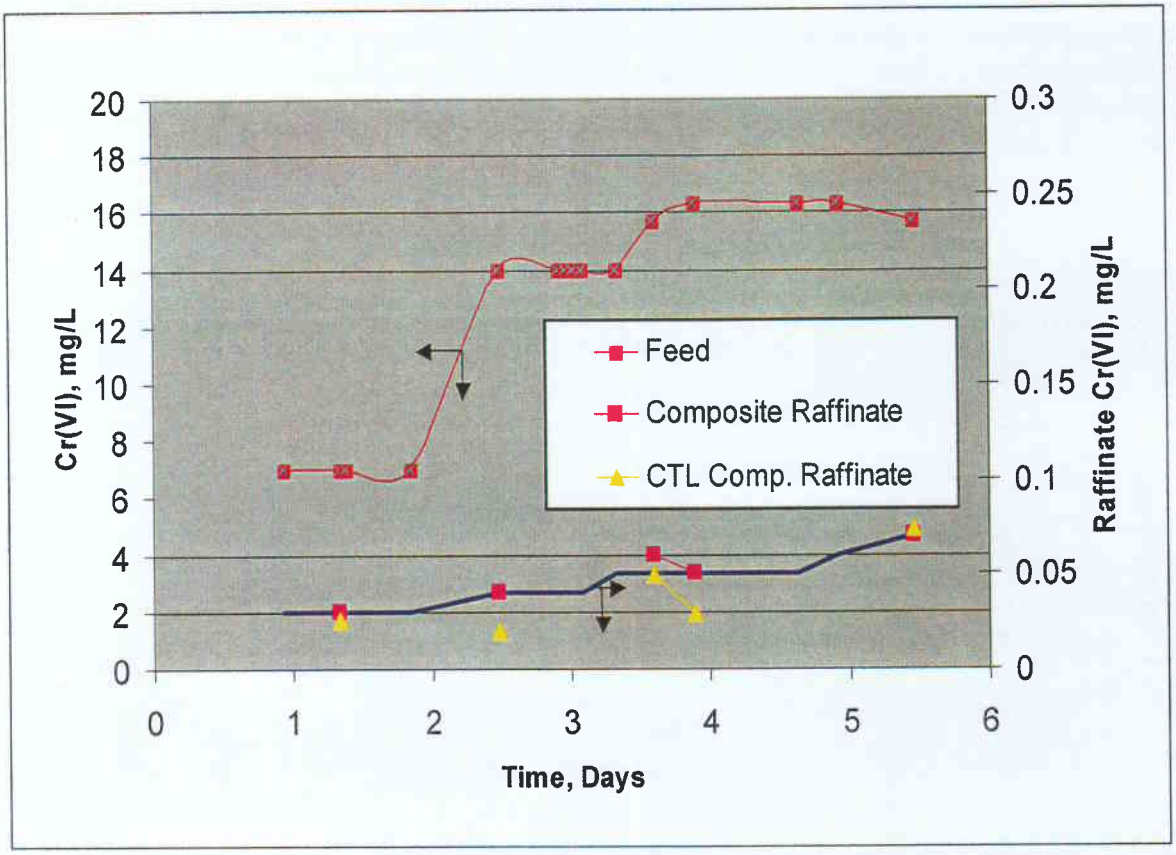


Figure 5-1. Run No. W-6 Feed and Raffinate Concentrations Versus Time

Table 5-1. Watervliet Run Results

Parameter	Run No. W-6	Run No. W-7
Feed conditions	6 gal/min; 12. 8 ppm Cr (VI)	7 gal/min; 16 ppm Cr (VI)
Aqueous/Extractant (A/E) ratio	6/1	6/1
pH	2.7 E (Extractor); 12.9 S (Stripper)	2.7 E, 13.4 S
Cr (VI) in Extractor 1	0.86 ppm (93% extraction)	1.71 ppm (89% extraction)
Cr (VI) in Extractor 2	0.16 ppm (84% extraction)	0.40 ppm (66% extraction)
Cr (VI) in Extractor 3	0.11 ppm (31% extraction)	0.19 ppm (53% extraction)
Cr (VI) composite raffinate	0.04 ppm (99.7% overall extraction)	0.23 ppm (98.6% overall); 0.11 ppm (99.4%) over days 14 - 18 after Alamine® 336 level fortified
Cr (VI) in Stripper–1	4,000 ppm (300 X concentration)	12,000 (800 times concentration)
Organics entrainment in raffinate as measured by oil and grease	76 mg/L[(a)]	119 mg/L[(a)]

(a) High O/G figures obtained due to very low operating temperatures.

Run W-7: As noted in Figure 5-2, this 20 days test operated for 24 hr/day demonstrated the system robustness and consistent performance operation with the strippers at high (10,000 to 15,000 ppm) Cr (VI) concentrate levels (also see Table 5-1 presented earlier). Steady operation over long periods is clearly illustrated. Various operational modifications were tested. The impact of these changes on raffinate Cr (VI) residual levels correlate well. Gradual extractant losses were made up at day 14 resulting in improved performance.

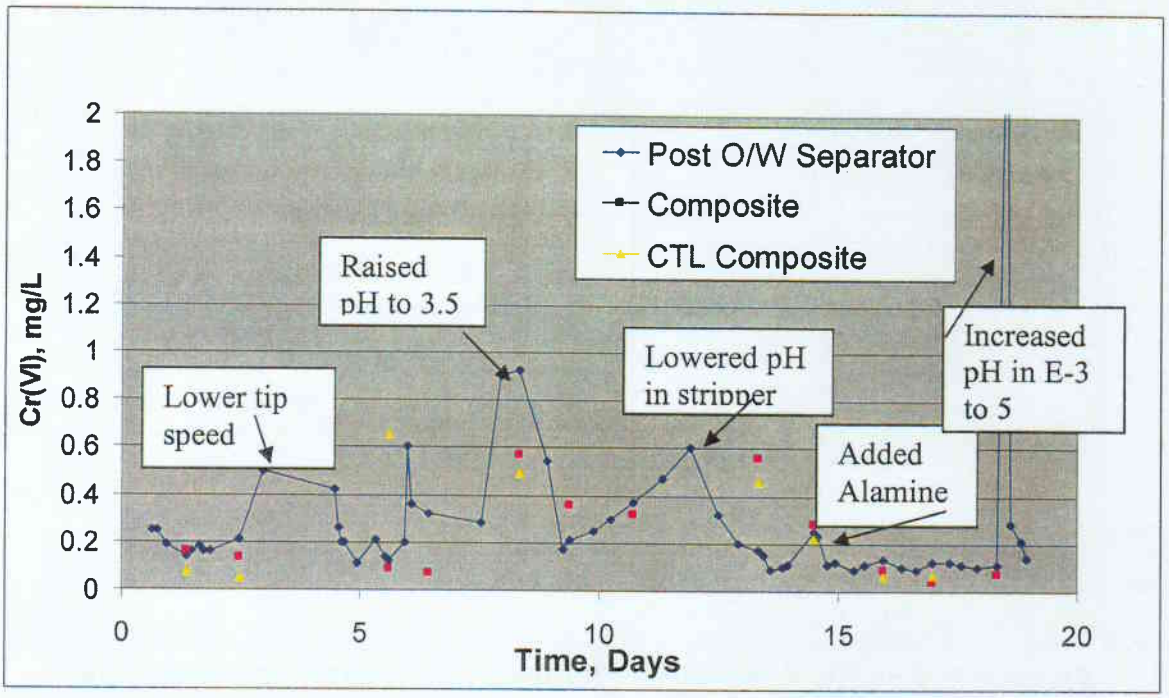


Figure 5-2. Run No. W-7 Rafffinate Cr (VI) Levels as a Funciton of Time.
Note Feed Cr (VI) Level Ranges from 11 to 22 ppm

Figure 5-3 shows photos of the feed material and the raffinates produced in extractor (E) Numbers 1, 2, and 3. The yellow Cr (VI) color of the feed is removed across the process, giving a clear and colorless raffinate.

Figure 5-3. Feed and E-1, E-2, and E-3 Raffinates

The raffinate analyzed sufficiently low in Cr (VI) for direct discharge.

Raffinate entrainment and turbidity levels are presented in Figure 5-4. The O/G levels were similar to W-6. Entrainment losses were higher than desired, but expected based on the water solubility of the protonated extractant. The turbidities were excellent, <7 NTU. It is believed that the extractant is dissolved in the raffinate as the cationic (protonated) species, R_3NH^+. The fully operational plant may adjust the pH of the raffinate to produce neutral R_3N, which will reduce its water solubility substantially. The IWTP already makes such a pH adjustment. Alternatively, the temperature of the water can be raised to lower oil and grease levels in the raffinate.

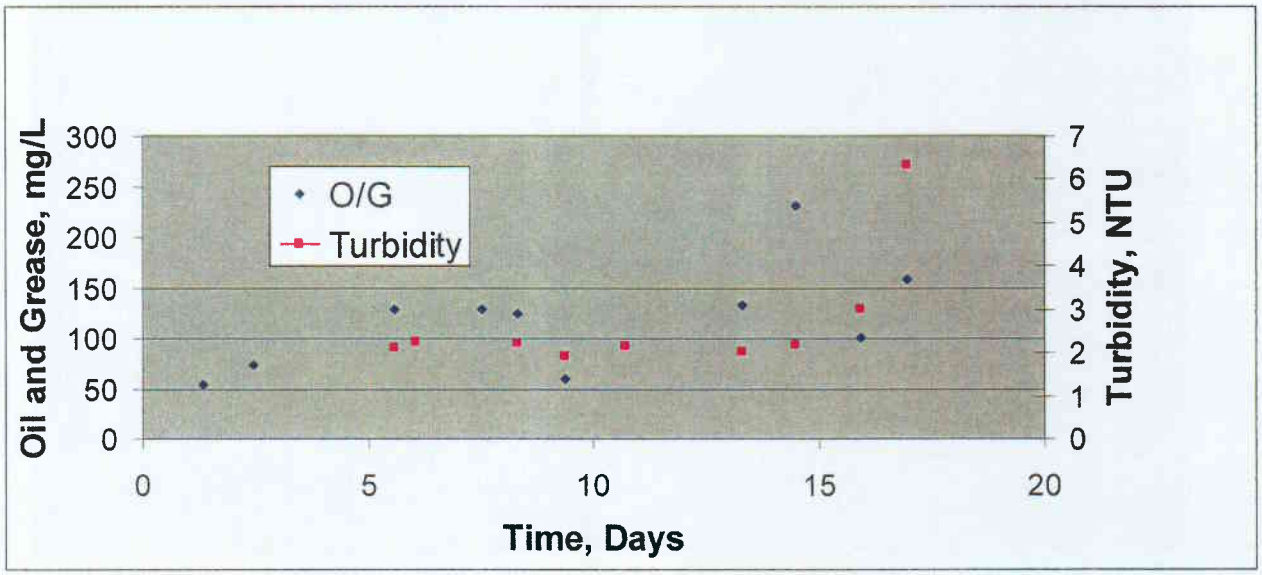


Figure 5-4. Run No. W-7 Entrainment as Measured by Oil and Grease and Clarity as Measured by Turbidity

Full metals analyses for the feed and raffinate are presented in Table 5-2. It shows that the A-LIX process did not, as expected, extract most positively charged metal cations such as As, Ba, Cd, etc. However, the process did remove much of the Cr (III) and nearly all the Cr (VI) from the feed water.

Table 5-2. RCRA Metals Analysis For WAA Feed and Raffinate

RCRA Metals and Hazardous Waste Regulation Limit, mg/L	Concentration, mg/L (~ ppm)				
	Plating Solution	Feed Water Created by Diluting Plating Solution	Raffinate	Monthly Discharge Limit at Watervliet	Monthly Discharge Limit at WR-ALC
Arsenic (5.0)	0.19	<0.002	<0.002	No limit	No limit
Barium (100)	<0.50	<0.50	<0.50	6	No limit
Cadmium (1.0)	1.05	<0.05	<0.05	0.15	0.1
Chromium (5.0)	73,300	15.2	0.64	3	0.3
Cr (VI)	17,440	8.7	0.02	0.3	No limit
Lead (5.0)	19.7	<0.20	<0.20	0.6	No limit
Mercury (0.2)	0.005	<0.001	<0.001	No limit	No limit
Selenium (1.0)	30.6	<0.005	0.0153	No limit	No limit
Silver (5.0)	1.66	<0.10	<0.10	No limit	No limit
pH	6	3	3	6 – 9	6 - 9

Figure 5-5 shows the clear yellow concentrated Cr (VI) product solution.

Figure 5-5. Photo of WAA Chromium Concentrate

The concentrate was analyzed and the results are summarized in Table 5-3. The 13,000 ppm Cr (VI) concentration was found to be an acceptable feedstock for production of Cr (VI)-based chemicals. Six 55-gallon drums of this material were produced for recycle process demonstration. Samples were submitted to Inmetco, a Cr recycler, for evaluation. Inmetco performed independent analyses and determined that the material was acceptable for recycle along with other metal oxides into the steel making process.

Table 5-3. Cr Concentrate Analysis

Parameter	Result (Average of 4 Readings)
Total organic carbon	460 mg/L
Fluoride	10 mg/l
Sulfate	7.6%
Sulfide	< 20 mg/L
Arsenic	<0.02 mg/L
Barium	< 5 mg/L
Cadmium	0.6 mg/L
Chromium	12,900 mg/L
Lead	4.5 mg/L
Mercury	0.01 mg/L
Selenium	0.026 mg/L
Silver	0.84 mg/L

Figure 5-6 represents a projected process flow diagram for a commercial 3-extractor, 2-stripper mixer/settler system for the nominal WAA conditions. The acid, base, raffinate, and Cr concentrate figures were based on test results. Over a seven-month period, data from the plating shop indicated an average flow rate of ~47,000 gal/day with a Cr (VI) concentration of 13 to 52 ppm[9]. In the demonstration tests, the simulated Cr (VI) rinse water was continuously contacted in countercurrent flow with the extractant to remove Cr (VI) from the aqueous effluent to produce clean water with discharge concentrations below 0.1 ppm. The Cr (VI) was concentrated to 13,000 ppm, representing a viable chromium source for recycle and reuse.

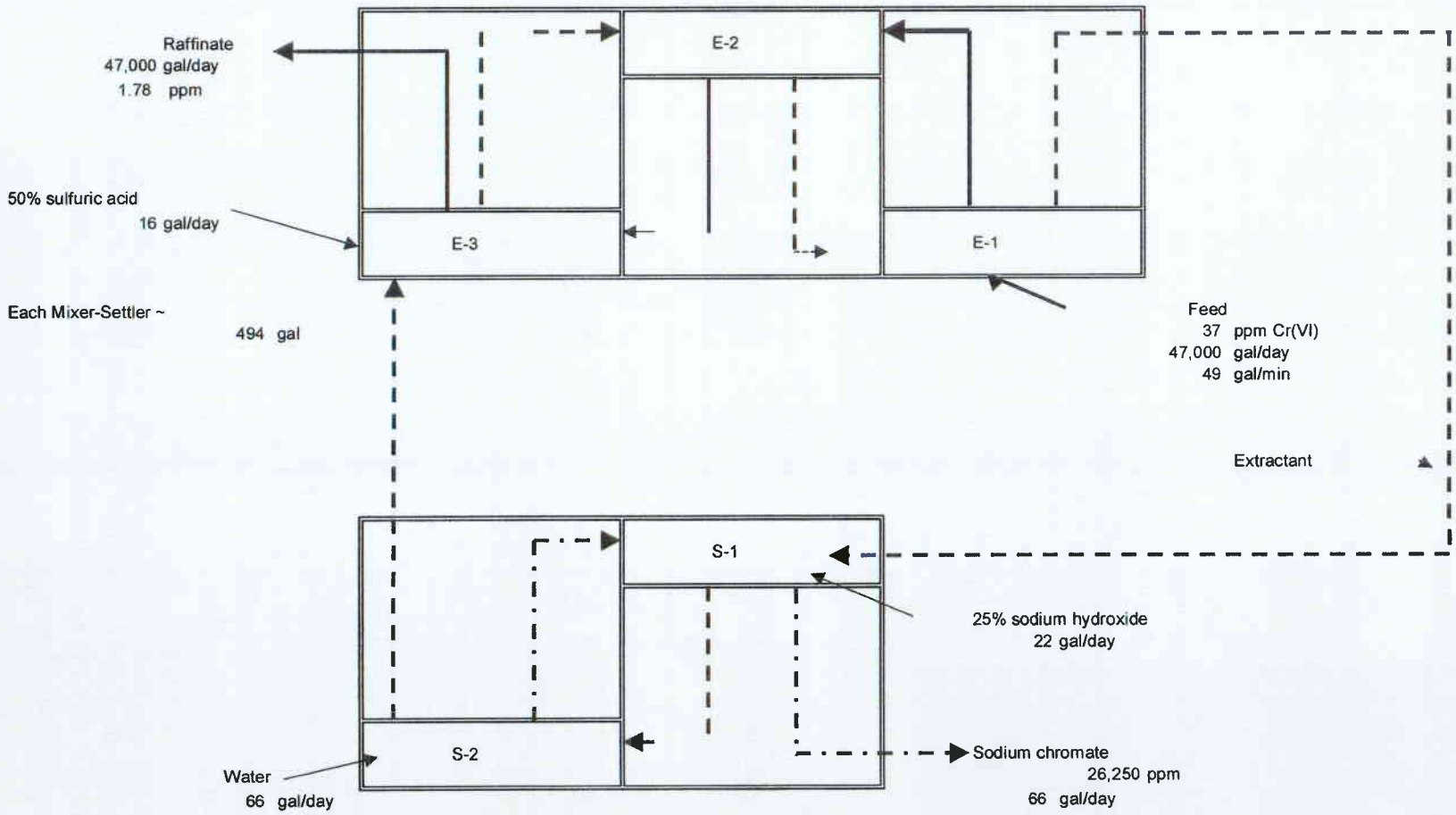


Figure 5-6. Projected Full-Scale A-LIX System Performance for WAA

5.1.2 Warner-Robins Air Logistic Center Performance Data . The WR-ALC testing using the Cr-contaminated wastewater from the Building 142 plating shop processed about 100,000 gallons (0.4 million liters) of feed during the two runs with the following results.

Runs No. R-1: This start up run established the primary operating conditions, i.e., feed rate, E/A flow ratio, stirrer tip speeds, and pH control was also suitable for WR-ALC operation. After this testing, sodium chromate was added to the strippers to increase the Cr concentration to typical steady-state level of 10,000 ppm of Cr (VI).

Run No. R-2: This extended duration run demonstrated operability, extraction performance, robustness, and consistent performance over 20 days at 12 to 24 hr/day operation with the strippers with 4,000 to 22,000 ppm Cr (VI) concentrate levels.

Run Nos. R-1 and R-2 results are summarized in Table 5-4 and Figure 5-7. Steady operation over the entire period was clearly illustrated. Gradual extractant losses were made up after day 13.

Oil and grease figures are shown in Figure 5-8 (excluding one outlier). Raffinate entrainment, as measured by oil and grease were significantly lower than in the WAA testing. The difference was attributed to the higher wastewater temperatures (~ 100 to 110 F).

Table 5-4. WR-ALC Run Results

Parameter	Run No. R-1	Run No. R-2
Feed conditions	6.8 gal/min; 55.0 ppm Cr (VI)	6.9 gal/min; 7.6 ppm Cr (VI)
Aqueous/Extractant/ (A/E) ratio	8/1	7/1
PH	2.7 E (Extractor); 13.4 S (Stripper)	2.7 E (Extractor), 13.3 S (Stripper)
Cr (VI) in Extractor 1	6.8 ppm (88% extraction)	2.0 ppm (74% extraction)
Cr (VI) in Extractor 2	1.8 ppm (73% extraction)	0.7 ppm (63% extraction)
Cr (VI) in Extractor 3	0.8 ppm (57% extraction)	0.2 ppm (73% extraction)
Cr (VI) composite raffinate	0.8 ppm (99.2% overall extraction)	0.17 ppm (98.9% overall)
Cr (VI) in Stripper –1	21,000 ppm (3,200 time concentration)	11,000 ppm (1,900 time concentration)
Organics entrainment in raffinate as measured by Oil and Grease	27 mg/L	5 mg/L

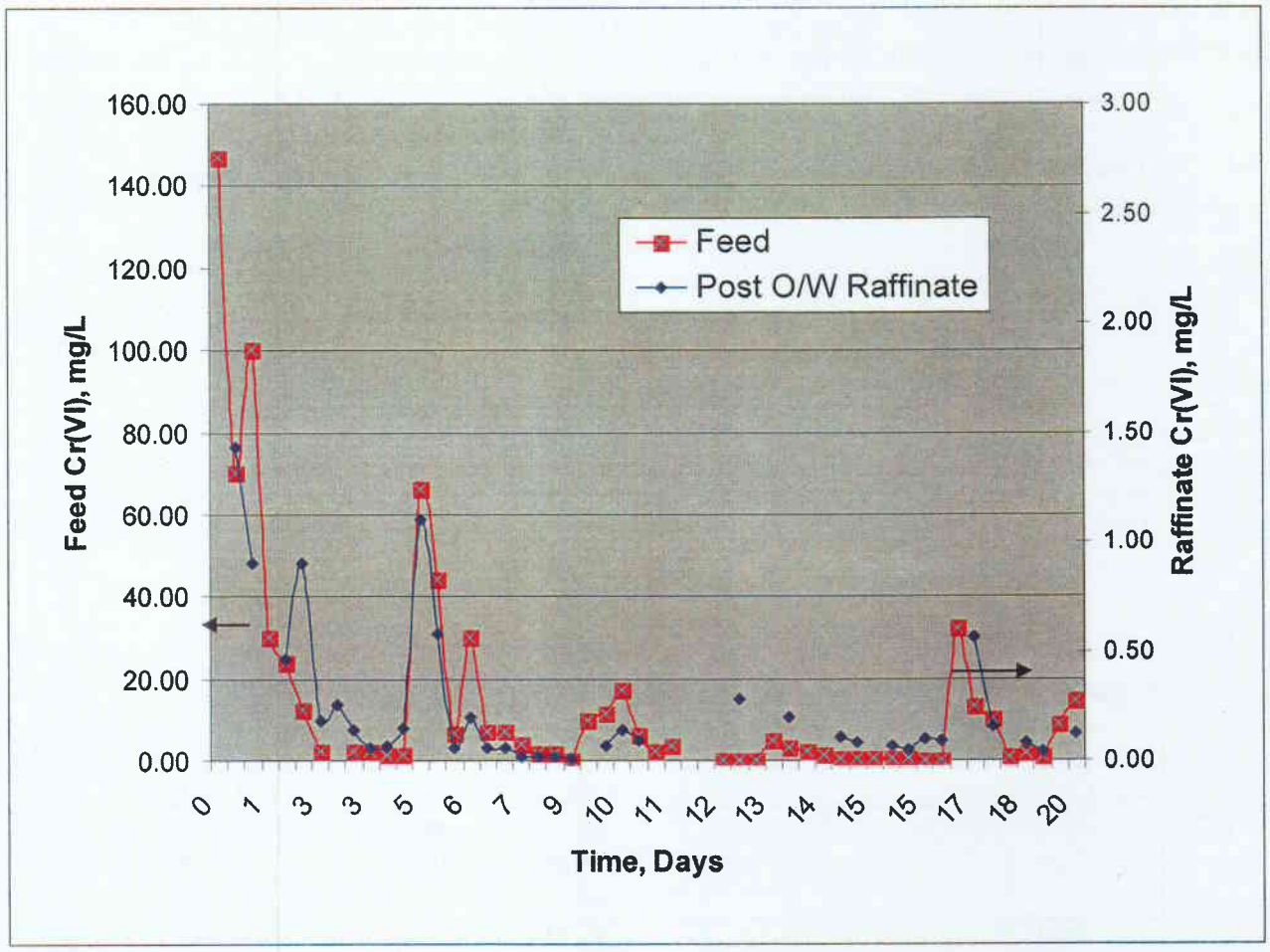


Figure 5-7. Cr (VI) Versus Time for Run No. R-2
Excludes data for day 9 where pH of feed was ~ 1

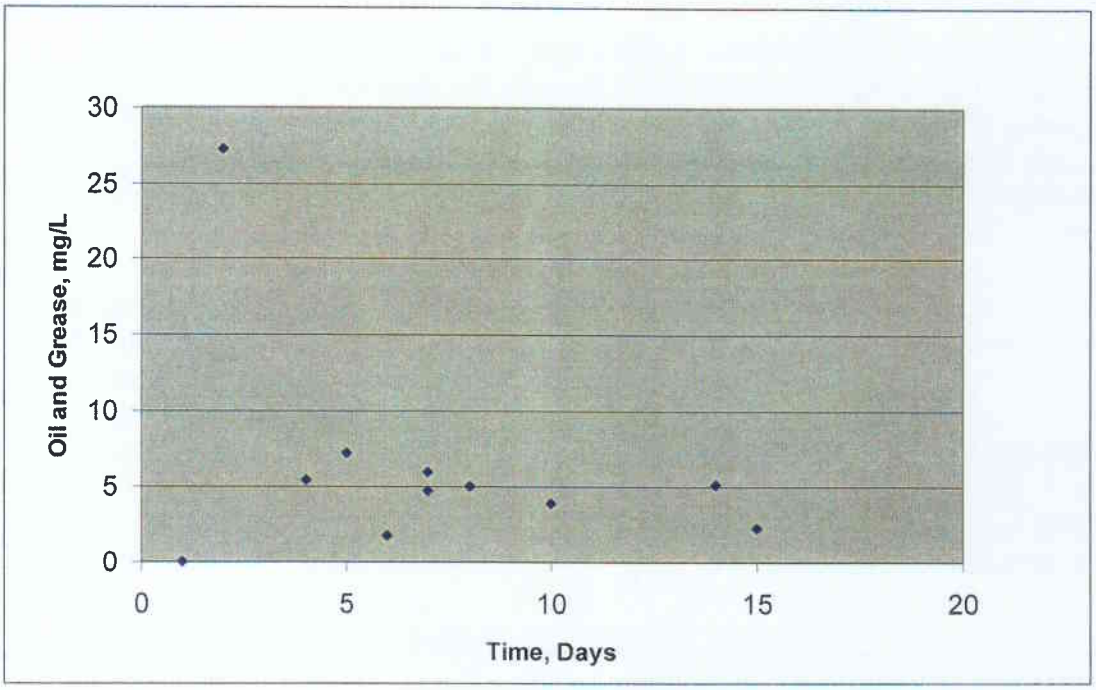


Figure 5-8. Oil and Grease Levels for Run No. R-2

Full metals analyses for the feed and raffinate are presented in Table 5-5. They show that the A-LIX process did not extract most positively charged metal cations. However, like in the WAA test series, the process did remove much of the Cr (III) and nearly all the Cr (VI) from the feed water.

Table 5.5 RCRA Metals Analysis For WR-ALC Feed and Raffinate

Metals (Hazardous. Waste Regulation Limit, mg/L)	Concentration, mg/L (~ ppm)			
	Feed Water	Raffinate	Monthly Discharge Limit at Watervliet	Monthly Discharge Limit at WR-ALC
Chromium (5.0)	19.7	1.62 [(a)]	3	0.3
Cr (VI) (No limit)	NA	0.25	0.3	No limit
Iron (No limit)	5.6	1.90	No limit	No limit
Nickel (No limit)	0.06	0.04	No limit	No limit
Copper (No limit)	0.10	0.08	No limit	No limit
Zinc (No limit)	0.69	0.64	No limit	No limit
Lead (5.0)	0.05	0.06	0.6	No limit
Cadmium (1.0)	0.05	0.03	0.15	0.1

(a) Total Cr levels before precipitation and removal.
(b) Indicates a Cr (VI) extraction level of 99.4%.
(c) Indicates a Cr (III) extraction level of 83%.

In the WR-ALC testing at 5,000 to 10,000 gal/day, the Cr (VI) rinse water was continuously contacted in countercurrent flow with the extractant to remove Cr (VI) from the aqueous effluent to produce clean water with discharge concentrations below 0.3 ppm. The Cr (VI) was concentrated up to 20,000 ppm (about 2000 to 3000 x concentration). This represents a viable chromium source for recycle into the steel industry.

Figure 5-9 illustrates a process flow diagram for a commercial 3-extractor, 2-stripper mixer/settler system based on the test performance and typical WR-ALC flow and feed concentration figures at the IWTP servicing the WR-ALC plating shop. Over the period Oct 99 through Jan 00, flow ranged from 37,000 to 72,000 gal/day (40,000 gal/day average) and Cr (VI) concentration ranged from 1.8 to 7.6 ppm (5 ppm average).[7]

5.2 Data Assessment

5.2.1 Performance Criteria. The performance criteria are listed in Table 5-6.

Table 5-6. ESTCP Performance Criteria

Performance Criteria	Description	Primary or Secondary
Hazardous Contaminant	Reduction of Cr (VI) concentrations in the process water to meet the 0.3-ppm target.	Primary
Concentrate Production	Produce a Cr (VI) concentrate having a concentration on the order of 20,000 ppm.	Primary
Process Economics	Validate full-scale economics with target payback period of less than three years.	Primary
Reliability	Breakdowns are not expected, but spare parts will be on hand. (The materials of construction are suitable for extremely high acid, base, and Cr concentrations, therefore it is not anticipated that handling the process fluids will lead to corrosion problems.)	Primary
Ease of Use	A qualitative assessment of the system's ability to run with little human supervision will be made.	Secondary
Maintenance	Little routine maintenance will be required.	Secondary
Process Waste	Generation of process wastes (little anticipated assuming the sodium chromate concentrate can be sold or recycled).	Secondary
Factors Affecting Technology Performance	The Cr (VI) concentrate produced may reach a concentration limit that could influence the system performance. No tests beyond 20,000 ppm are planned.	Secondary
Versatility	The A-LIX plant will be a mobile system that can be easily transported to various sites.	Secondary
Scale Up	No further scale up required, beyond the demonstration testing, prior to commercial implementation.	Secondary

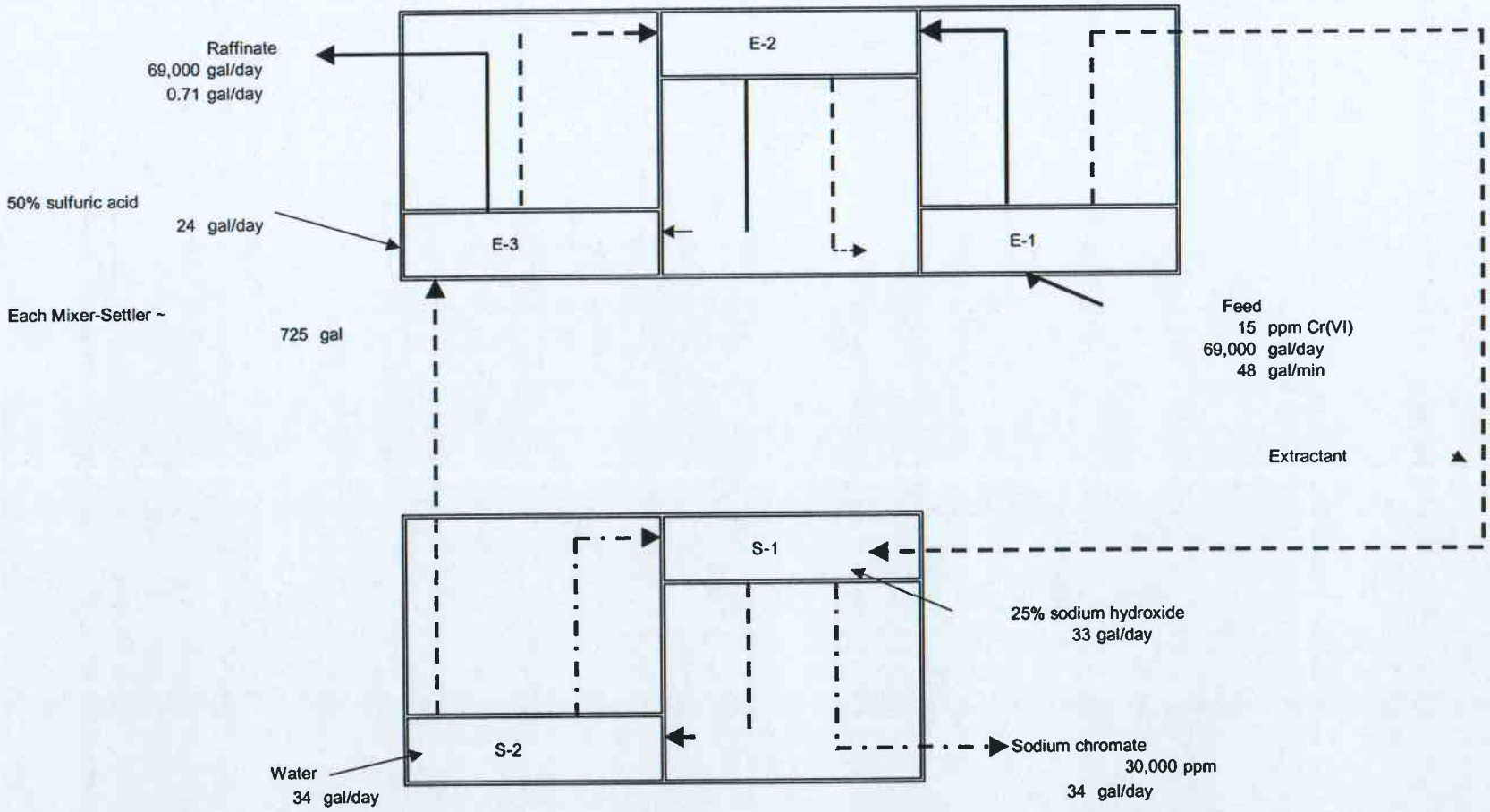


Figure 5-9. Projected Full-Scale A-LIX System Performance for WR-ALC

5.2.2 Performance Assessment. The effectiveness of the A-LIX system was evaluated against the performance parameters presented in Table 5-6. As noted in Table 5-7, the operations met all performance criterion elements except Alamine® 336 content in the raffinate. There was some uncertainly in the accuracy of this parameter. Overall, the unit performance was considered a success.

Table 5-7. Expected and Actual Performance

Performance Criteria	Performance Confirmation Method	Expected Performance	Actual Performance
Effluent stream Contaminant concentration (after treatment)	Hach diphenyl-carbazide colorimetric method	<0.3 ppm Cr (VI)	≤0.3 ppm whenever feed Cr (VI) levels were below 30 ppm
Concentrate produced	Hach diphenyl-carbazide colorimetric method	>20,000-ppm Cr (VI)	15,000 to 20,000 ppm Cr (VI) as sodium chromate
Total Cr	Atomic absorption	<0.3 ppm Cr if no Cr (III) in feed	All tests found that there were significant Cr (III) in the feed and in the raffinate
Residual oil	Oil and grease	<50 ppm	~5 ppm when the feed water temperature was elevated
Alamine® 336	Modified Henkel Extraction test [(a)]	<5 ppm	<1 ppm based on oil and grease figures; or 25 ppm based on Henkel test
Cost	Cost calculation	<3 year payback	2.4 to 3.9 years
Reliability	Record keeping	Achieve multi-day uninterrupted operation	Achieved
Ease of use	Experience from demonstration operations	No excessive maintenance or operating labor requirements	Achieved
Versatility of mobile system	Experience from demonstration operation	Ease of shutdown, transport, and startup	Shutdown and moved in 5 days

(a) Colorimetric method developed by Henkel for the "Colorimetric Determination of Alamine® 336 in Solvent Extraction Raffinates and Pulps" as modified by CTL.

5.3 Technology Comparison

There are four primary methods for conventional treatment of Cr (VI) contaminated plating-shop wastewater. All involve Cr (VI) reduction followed by precipitation of the metal hydroxides using NaOH. The four methods vary in the pH required for treatment, the choice of reductant, and amount of sludge produced. Use of the A-LIX process eliminates the need for reductant chemicals, eliminates the production of Cr (VI)-metal hydroxide sludge, avoids the need to handle highly toxic chemicals, avoids long-term liability problems (related to the production of sludge), and provides a means to recycle the Cr back into a useful product.

The costs of the A-LIX process were compared with the cost for conventionally reduced and precipitated technologies at WAA and WR-ALC. Results are shown in Section 6.

6. Cost Assessment

6.1 Cost Reporting

Cost issues are critical to the evaluation of the A-LIX process. Battelle estimated capital and operating costs of a full-scale commercial A-LIX facility. Battelle completed a pseudo Level II cost assessment of both the existing Cr treatment technology and the A-LIX process using a modified version of the Environmental Cost Analysis Methodology (ECAM). A cost estimating procedure was followed to identify, quantify, and assign environmental costs to the baseline and A-LIX process for WAA and WR-ALC.

The following assumptions were included in this analysis:

- Capital costs for larger-scale A-LIX facilities can be estimated from the $140,000 cost for the 7 gpm unit by assuming a scale-up factor of 0.46; i.e., $140,000 times (new capacity/7 gpm) raised to the 0.46 power. To this cost is added $50,000 for installation and 12% of the capital plus installation for utility connections.
- The feed is assumed to be 2/3 Cr (VI) and the balance is Cr (III).
- Extraction efficiency is 99.3% for Cr (VI) and 80% for Cr (III)
- Extractant ratio is 90/5/5 for Conoco® 170 ES, Alamine® 336, and Exxal® 10.
- Costs are $2.65/gal of Conoco® 170 ES, $19.96/gal of Alamine® 336, and $5.67/gal of Exxal® 10.
- The desired A-LIX feed water pH was 3. The experimental H_2SO_4 utilization rate was 1.7 lb of 50% H_2SO_4/10,000 gal of feed water (0.35 gal of 50% H_2SO_4/Kgal). This rate was used for costing purposes. A feed pH of 4 can be utilized if the Alamine® 336 is increased to 20% (from the normal 5% level) in the extractant; this could reduce the H_2SO_4 utilization rate by approximately 20%.
- The desired A-LIX stripper pH level was 13. The experimental NaOH utilization rate was 2.1 lb of 25% NaOH/10,000 gal of feed water (0.475 gal 25% NaOH/Kgal). This rate was used for costing purposes. When a feed pH of 4 is utilized the required quantity of NaOH can be decreased by about 20%.
- Cost for H_2SO_4, NaOH, coagulant/floc aids and polymers were based on WAA and WR-ALC specific rates.
- Labor rates were based on WAA and WR-ALC specific rates. Savings in labor were based both on IWTP and sludge handling/dewatering labor savings.
- An overhead rate of 80% was added to all the labor charges.
- Training, compliance audits, testing of liquids and solids, medical exams and loss of productive time, etc. were based on WAA specific rates and estimated for WR-ALC.

- Losses of extractant are based on a 5 ppm overall loss rate (based on the 5 ppm O/G figure determined at WR-ALC), losses of Conoco® 170 ES, and Exxal® 10, 4, and 0.25 ppm, respectively. The loss of Alamine® 336 was estimated at 25 ppm (based on chemical analysis); the 25-ppm loss figure was used for cost estimation.
- The raffinate produced by the A-LIX process has a pH of between 3 and 4; the extra NaOH required to increase the pH to the 3 to 6 level normally experienced at the base IWTPs represents only a few thousand dollars/year and was ignored.
- The reduction in the sludge production rate was directly proportional to the reduction in the total Cr discharged by the A-LIX system, i.e., the 92% decrease to total Cr resulted in a reduction in sludge production by 92%. Any extra NaOH required to increase the raffinate pH to the normal feed level would not result in any increase in sludge production.
- Particulate matter in the wastewater removed upstream from the A-LIX unit would be transferred to the IWTP hazardous waste disposal area with no net charge to the A-LIX system.
- Other wastes such as rag layers are only generated during shutdown and movement of the equipment; there is no charge assigned as shutdown and movement would not be a normal operational activity.
- The Cr concentrate was shipped to Inmetco for recycle. A recycle charge of $1/gal and a transportation charge of $1/ton-mile were applied. No other recyclers were identified.

The costs for sludge disposal were based on WAA and WR-ALC practices; a transportation charge of $1/ton-mile was applied for WR-ALC.

6.2 Cost Analysis

A summary of the projected A-LIX capital and operating costs is reprovided in Table 6-1 for WAA and WR-ALC. The startup, operating and maintenance, indirect environmental and other associated costs for A-LIX facilities at WAA and WR-ALC are detailed in Table 6-2. Treatment costs per 1,000 gallons of wastewater were $17.50 and $19.90 for WAA and WR-ALC, respectively.

Table 6-1. A-LIX Cost Summary

Parameters	A-LIX Capital Costs, $K	
	WAA	WR-ALC
Total capital	491	449
	Annual Costs, $K/year	
Operating and maintenance	200	300
Indirect environmental	28	58
Other	72	142
Total annual costs	300	501

Table 6-2. A-LIX Capital and Operating Costs

Start-Up			Operating and Maintenance			Indirect Environmental Activity Costs			Other Costs		
Activity	Cost, $K/year		Activity	Cost, $K/year		Activity	Cost, $K/year		Activity	Cost, $K/year	
	WAA	WR		WAA	WR		WAA	WR		WAA	WR
Facility preparation, mobilization	53	48	Labor to operate equipment	64	138	Compliance audits			Overhead assoc. with Process		
Equipment design			Labor to manage hazardous waste	26	26	Document maintenance			Productivity/ cycle time		
Equipment purchase	388	351	Utilities	5	7	Envir Mgmt Plan Dev & maintenance			Worker injury claims and health costs	72	142
Installation			Mgmt/ Treatment of by-products	(a)	14	Reporting requirements	8	20			
Training of operators	50	50	Hazardous waste disposal fee	15	14	Test/analyze waste streams	3	18			
			Process chemicals	29	37	Medical exams (including loss of productive time)	1	1			
			Consumables and supplies	8	8	Waste transportation (on and off site)	16	16			
			Equipment maintenance	53	51	OSHA/EHS training	1	4			
			Training of operators	1	5						
			Subtotal	200	300	Subtotal	28	58	Subtotal	72	142
Total Capital	491	449							Total Operating and Environmental	300	501

(a) Included with waste sludge handling costs.

6.2.1 Cost Drivers. The cost drivers included (1) capital cost, (2) operating labor requirements, (3) chemical costs, (4) laboratory requirements, and (5) disposition cost of the Cr (VI) concentrate.

6.2.2 Life Cycle Cost Comparisons

The life-cycle costs of the Cr (VI) treatment processes were calculated based on the following considerations: (1) facility capital cost, (2) startup, operations and maintenance, and demobilization costs, (3) equipment replacement costs, and (4) environmental compliance costs. A 10-year time period was used for the life-cycle period for cost comparison. The base case operating costs for conventional Cr (VI) treatment as practiced by WAA and WR-ALC were estimated at $426K and $691K/year, respectively. Details of the conventional IWTP costs are provided in Table 6-3. A comparison of the projected financial performance is noted in Table 6-4. Financial indicators included payback period, net present value (NPV), and internal rate of return (IRR).

Table 6-3. IWTP Costs

Operating and Maintenance			Indirect Environmental Activity Costs			Other Costs		
	Costs, $K/year			Costs, $K/year			Costs, $K/year	
Activity	WAA	WR	Activity	WAA	WR	Activity	WAA	WR
Labor to operate equipment	127	191	Compliance audits	9	23	Overhead associated with process	123	203
Labor to manage hazardous waste	26	26	Document maintenance			Productivity/ cycle time		
Utilities	6	9	Environmental Management Plan development and maintenance			Worker injury claims and health costs		
Management/ Treatment of by-products	--	36	Reporting requirements					
Hazardous waste disposal fee	44	40	Test/analyze waste streams	3	35			
Process chemicals	17	42	Medical exams (including loss of productive time)	0	1			
Consumables and supplies	9	9	Waste transportation (on and off site)	--	9			
Equipment maintenance	60	60	OSHA/EHS training	1	4			
Training of operators	1	4						
Subtotal	290	416	Subtotal	13	72	Subtotal	123	203
Total							426	691

Table 6-4. Cost Comparison: Conventional Treatment Versus A-LIX

Parameter	WAA	WR-ALC
Conventional Performance		
Annual costs, $/year	426	692
A-LIX		
Annual costs, $/year	300	501
Projected savings, $/year	126	191
A-LIX startup capital and training costs, $K	491	449
A-LIX Performance		
Payback period, years	3.9	2.4
Net present value, $K, at 8% annual discount rate and 10 year life, $	355	830
Internal rate of return, 10 year, %	22%	41%

In general, payback periods of less than 3 years, a positive NPV at the noted discount rate, and an IRR of >10 % indicates a very good investment. For both WAA and WR-ALC, the analysis indicates that installation of an A-LIX system would provide very good economic payback.

The WAA operations are not as favorable as WR-ALC, based on payback period and IRR. The lower performance indicators were due to lower labor and sludge handling/disposal costs in the conventional WAA treatment system compared to WR-ALC. Therefore, the improvements allowed by use of an A-LIX system are not as dramatic in the WAA case. The economic performance parameters are still very good, and an A-LIX application at WAA is still economically justified.

7. Regulatory Issues

7.1 Approaches to Regulatory Compliance and Acceptance

7.1.1 Environmental Checklist. Because of Battelle's role in research and development, short-term testing US EPA permits were not required. However, a Battelle "discharge to drain" permit as described in Battelle's EN-PC-02.0 Discharge to Drain Procedure was followed for testing at Battelle. The City of Columbus allows a discharge level of 1.9-ppm total Cr [Cr (III) +Cr (VI)] maximum composite sample concentration. Since we achieved a < 1 ppm discharge level, this was not a problem. The City also states that the hydrocarbon/ /fat/oil/grease discharge cannot exceed 200 ppm. Again since we achieved a 50 to 150 ppm level, this was not a problem. The demonstration plant at WR-ALC did not significantly change the amount of Cr entering and leaving the IWTP. Therefore, no new permits were required.

At WR-ALC, an AF Form 813 was required. This form served to notify impacted individuals and organizations of changes in the process treatment procedure.

7.1.2 Other Regulatory Issues. Battelle obtained the assistance of Mr. Dave Ferguson of the US EPA (Cincinnati office). Mr. Ferguson specializes in new controls/innovations affecting the plating shop industry. Battelle sought his guidance regarding new regulations on the discharge of Cr contaminated wastewater generated in Cr plating shops during two briefing meetings over the course of the program.

Currently the federal regulations, 40CFR 433.10 (Metal Finishing), only limits the total Cr discharge rate. The effluent concentration limit is <1.71 mg/L total chrome. Local regulations can be much more restrictive. Requirements for WAA were:

- 3.0 lb total Cr/day and 0.3 lb Cr (VI)/day
- 6 mg/L (ppm) daily average total Cr and 0.6 mg/L Cr (VI) based on 58,000 gpd of Cr contaminated wastewater.

For WR-ALC, the State of Georgia, Department of Natural Resources Authorization to Discharge under the NPDES restricts the discharge at IWTP No. 2 to:

- 1.2-lb total Cr/day daily average [1.7-lb total Cr/day daily maximum] as total Cr.
- 0.30-mg/L daily average [0.45-mg/L daily maximum] as total Cr.

There are no specific Cr (VI) regulations at WR-ALC.

The raffinate produced by the A-LIX process has a pH of between 3 and 4. The low pH of the raffinate is not expected to detrimentally affect IWTP operations. The extra NaOH required increasing the pH to the 3 to 6 level normally experienced at the base IWTPs represents only a few thousand dollars/year and was ignored in the cost analysis in Section 6.2.

At Battelle, the O/G level was ~50 ppm. The Alamine® 336 might constitute 5% to 10% of O/G or up to 5 ppm. Alamine® 336 at high concentrations is toxic to aquatic wildlife and could present a problem for downstream biological sewage treatment. This was not a problem at Battelle because the 10,000 gpd discharge of Cr raffinate from the A-LIX process was diluted with 200,000 gpd of wastewater from other uses. Thus, it was reduced to well below 1 ppm prior to leaving the Battelle property.

It was also not a problem at WR-ALC where the A-LIX discharge O/G level was ~ 5 ppm. The 10,000 gpd discharge of Cr raffinate from the A-LIX process was diluted with 50,000 to 70,0000 gpd of acid/alkali wastewater then subjected to neutralization with NaOH, flocculated, thickened, and the treated water discharge to the river. There it is diluted with over a million gpd of clean water produced from WR-ALC combined sanitary and industrial wastewater treatment plants. Therefore, it is not anticipated that there would be any required changes to the WR-ALC NPDES permit.

The discharge of the Conoco® 170 ES should be treated like any other O/G constituent of the wastewater. No adverse impact to the IWTP operation was experienced.

8. Technology Implementation

8.1 DoD Need

Chromium (Cr) is widely used within DoD and industry for critical metal plating, corrosion control, and surface finishing requirements. However, the hexavalent Cr (VI) anion is toxic and must be removed from wastewaters prior to discharge. The current technology to remove Cr (VI) involves Cr (VI) reduction to Cr (III) followed by precipitation. While the precipitation process is effective, it generates large amounts of hazardous sludge. These sludges represent the single largest type of hazardous waste at many DoD maintenance facilities. As noted in Table 8-1, it has been estimated by Battelle, based on AF-ALC data, that about 1,960 tons per year of hazardous sludges are generated by the DoD primarily as a result of efforts to curtail Cr (VI) discharges.[1]

Table 8-1. Chromium Hydroxide Sludge Production

Chrome Hydroxide Sludge Produced from DoD Installations, by Site, ton/year		
Robins AFB (WR-ALC)	Hill AFB (OO-ALC)	DoD Wide (Based on 14 installations)
186	100	1,960

The high cost of handling Cr (VI) in wastewater and the associated sludge generation is a key reason behind several DoD needs lists (e.g., 101, 816, and 541 for Air Force) for eliminating Cr (VI) use[2]. While DoD and others are evaluating alternatives to Cr (VI), it is still the material of choice for corrosion resistance. Until all use of Cr is eliminated, there will be Cr discharges. Therefore, an improved Cr (VI) removal technology is needed.

8.2 Transition

Transition issues are addressed in Tables 8-2 through 8-7. The next step required for the implementation of the technology is summarized in Table 8-2.

Table 8-2. Next Step in Technology Implementation

Questions	Answers
What is the next step for the A-LIX technology?	A full-scale A-LIX for 60,000 to 100,000 gal/day is being designed for use at Hill AFB (near Salt lake City, UT)
Will it need more demonstration?	Site specific testing may be advisable to convince local authorities of the value and effectiveness of the technology
Will it need regulatory approval?	Regulatory approval may be required at each site to ensure compliance with the local NPDES permit requirements
Will it need additional funding?	Yes: for site specific testing, economic analysis and regulatory review
Will it need an industrial partner?	A relationship with Versatile Industries, the system fabricator that built the land/sea box mounted A-LIX demonstration unit, has been established

In Section 2.2, advantages and weaknesses in the A-LIX technology were discussed. The impact of these weaknesses and means to mitigate are summarized in Table 8-3.

Table 8-3. Weaknesses That Could Affect Technology Implementation

Questions	Answers
How will weaknesses be addressed? By Whom and when?	• The A-LIX process does not provide a complete solution to plating-shop wastewater treatment. A secondary caustic addition and metals precipitation, settling, and dewatering step is needed to remove cationic metals such as copper, cadmium, lead, etc. **Battelle will address this in a proposed new AFRL program to marry the A-LIX technology to a cation liquid-liquid extraction technology developed by Battelle.** • The recovered Cr cannot be used directly in the plating operations. **It may be possible to utilize a Battelle developed salt splitting technology to convert sodium chromate into NaOH and CrO_3. However, no plans are underway at this time to develop this technology.** • The recovered Cr can be recycled into the metals industry, but at a charge of ~$1/gal in large quantities. In addition, the recovered Cr must be transportation to Pennsylvania for recycle. This is a weakness due to the charges for transportation and liability issues due to potential spills. **It may be possible to concentrate the sodium chromate to a higher concentration or crystallize out the salts prior to recycle. This would decrease recycle costs and transportation costs. Battelle will pursue as part of the current Hill AFB design program.** • The estimation of full-scale A-LIX plant costs was based on escalating the design, procurement, equipment, and installation costs for the 10,000 gpd land/sea box demonstration unit. Better data for significantly larger plants are needed. **Battelle will generate better capital cost estimates in the Hill AFB plant design, which is anticipated to process between 60,000 and 100,000 gpd.** • The clean water may not be sufficiently clean for direct recycle back to the plating shop. **Battelle will investigate on subsequent projects the ability to remove dissolved solids and oil and grease levels sufficient for water recycle.**

Deficiencies in meeting the program goals were discussed in Section 5.2.2 "Performance Assessment." Two potential deficiencies were noted. Methods to address these deficiencies are summarized in Table 8-4.

Table 8-4. Deficiency Affecting Technology Implementation

Questions	Answers
How will deficiencies be addressed? By Whom and when?	**1.** The cost effectiveness of the unit did not provide a payback period of less than 3 years in all applications (3.9 years at WAA and 2.4 years at WR-ALC). **This deficiency will be addressed by designing a more cost effective unit and gathering a better understanding of savings achieved via implementation of the A-LIX technology.** **2.** The Alamine® 336 content in the raffinate may not have met the ≤ 5 ppm goal. The Alamine® 336 content was estimated by two methods. o The first was based on O/G determinations: by this method the Alamine® 336 constituted about 5% of the 5 ppm O/G level (i.e., 0.25%) and therefore met the requirement. **Thus, by this method there was no deficiency.** o The second method was a Cognis (formerly Heckel Chemical Co. (the company that sells Alamine® 336) chlorinated hydrocarbon-extraction analytical procedure. Cognis no longer provides an analytical method to measure Alamine® 336 in water. The original Henkel procedure called for the use of carbon tetrachloride; but CCl_4 is no longer available. Therefore, Battelle instructed Columbus Testing Laboratory to use trichloroethylene instead. By this modified method, the Alamine® 336 content was ~ 25 ppm. However, the sensitivity of this method could not be confirmed using spiked samples. To be conservative, Battelle used the 25-ppm figure in the cost estimates. **Battelle checked with the base regulatory group, they determined that O/G was the only NPDES concern, and as the 5 ppm O/G figures was below the 15 ppm limit, there was no problem.**

The recommended path for implementation of the A-LIX technology is summarized in Table 8-5.

Table 8-5. Recommendations for Technology Implementation

Questions	Answers
Best implementation pathway?	Design and implement technology at Hill AFB. Once proved successful, design and implement unit at WR-ALC. Follow up at other DoD installations. Expand into the commercial plating shop market place.
How transferred to the user?	Through service contracts administered by Battelle
Is procurement guidance needed?	No

The level of industry involvement in the technology development and future implementation is summarized in Table 8-6.

Table 8-6. Industry Involvement in Technology Implementation

Questions	Answers
Was industry involved?	The first two potential users, WR-ALC and Hill AFB were involved throughout the program development and testing
Will industry be interested?	Both the DoD plating shop and commercial industry should be interested in the technology

The responsibility and projected timetable for the A-LIX implementation is noted in Table 8-7.

Table 8-7. Responsibility and Timetable for Technology Implementation

Questions	Answers	
Who is responsible for necessary actions?	Battelle	
Timetable		
Action	**Interested Parties**	**Date of Next Action**
Design commercial A-LIX plant for Hill AFB	Battelle	Work started in September 2001
Install commercial A-LIX plant for Hill AFB	Battelle/Versatile Industries	Tentative: Initiate mid FY02
Design commercial A-LIX plant for WR-ALC	Battelle	Tentative: FY03
Install commercial A-LIX plant at WR-ALC	Battelle/Versatile Industries	Tentative: FY03
Identify other implementation sites	Battelle	Tentative: Initiate mid FY02

9. Lessons Learned

1. Good working relationships between the Battelle technology development staff and AFRL, ESTCP, and the WAA and WR-ALC test site staff were critical to the successful development of A-LIX technology.
2. Good communications between the A-LIX staff and the IWTP staff was critical in overcoming scheduling, analytical, and operational problems.
3. Frequent meetings and consultation with the ultimate process owner (be it the Plating Shop or the Civil Engineering directorate) is critical to get "buy in" prior to technology implementation.
4. The attractiveness of the A-LIX technology must be analyzed on a case-by-case basis; local factors such as discharge limitations, labor utilization, chemical costs, and waste disposal practices can affect plant savings and thus the estimated payback period.

10. References

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9. Alice Fish. 2000. Private Communication. 24/August.

Appendix A
Points Of Contact

The points of contact are noted below:

Point Of Contact Name	Organization Name Address	Phone/ Fax/ Email	Role In Project
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Appendix B
Data Archiving and Demonstration Plans

B.1 Archiving Methods
The raw data from the demonstration tests are archived in the following Battelle Lab Record books:

1. 48737: WAA test notes
2. 300156: WAA testing raw data
3. 48874: WR-ALC test notes
4. 300157: WR-ALC raw data
5. 300158: analytical data.

B.2 Method to Receive Copy of Approved Demonstration Plan
The approved Dem/Val Plan can be obtained by:

1. Contacting Battelle's Dr. S. P. Chauhan at 614-424-4812 or H. Nick Conkle at 614-424-5616, or
2. Lt. Larry Cook at Tyndall Air Force Base at 850-283-6111, or
3. Robert Holst at ESTCP at 703-696-2117.