Recovery of Hexavalent Chromium From Plating Wastewaters Using A-LIX^{TM}

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A new commercial-scale plant using Battelle's anionic liquid ion exchange (A-LIX^{TM}) technology, an alternative treatment for surface finishing operations effluents has been installed in the hard-chrome plating shop of a Department of Defense facility. A-LIX^{TM} is an economic automated liquid-liquid extraction that recovers chromium from process wastewater, rather than generating metal-hydroxide sludge. This avoids costly disposal and the potential liability associated with disposal. The extractant is regenerated and reused in the process, resulting in low operating costs. This paper presents results from this ~57 million L/year (~15 million gallon/year) plant. Economic assessments, operational factors, and comparisons to conventional technology are presented.

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INTRODUCTION

Hexavalent chromium [Cr(VI)] is widely used within the military and industry to maintain dimensional tolerances, imparting corrosion and wear resistant properties, and other metal surface finishing (SURFIN) requirements. Cr(VI) is toxic and its control generates hazardous, costly waste[1]. Alternatives to chromium for the most demanding process applications have not been found. While federal regulation may remain unchanged, state regulators are constantly reviewing discharge limits. When these limits are lowered, many facilities may need to upgrade their rinse water management and treatment operations to meet new standards. A Cr(VI) recovery technology is needed to enable continued Cr use in these critical SURFIN processes.

Battelle's Anionic Liquid Ion eXchange (A-LIX^{TM}) system provides a unique Cr(VI) recovery technology for the Cr(VI) contaminated wastewater from the SURFIN industry. Battelle has developed and demonstrated the liquid-liquid extraction technology for removal of Cr(VI) from surface finishing wastewater and its concentration for recycle and recovery purposes[2-4]. The A-LIX^{TM} technology has been demonstrated to process rinse water from the hard chrome plating shop at Robins Air Force Base at the 38,000 L/day (10,000 gpd) scale and recently at a large hard chrome plating shop within a major Department of Defense (DoD) facility at a 163,000 L/day (43,000 gpd) scale. The process won an R&D 100 Award as one of the top new technologies for 2002. Based on data available from USEPA, Battelle estimates that between 550 to 600 SURFIN facilities in the USA discharge over 175,400 L/day (46,400 gpd) of chrome contaminated wastewater and could benefit from the A-LIX^{TM} system. This paper will focus on the recent start up experience of the full-scale A-LIX^{TM} plant for the hard chrome plating shop the major DoD facility.

A-LIX^{TM} PROCESS DESCRIPTION

The aqueous rinse water from the plating shop contains many metals. Cr(VI) is present principally as the bichromate anion, $HCrO_4^-$. The A-LIX^{TM} system employs a series of mixer/settlers to achieve a liquid-liquid extraction of the Cr(VI). The extractant phase is formulated by mixing commercially available chemicals. The extractant phase includes a selective extractant for Cr(VI), even over sulfate ion. Ion pairing is the primary extraction mechanism. The extractant is mixed with other organic diluents in the Battelle process. The Cr(VI)-loaded extractant is continually regenerated and recycled, keeping operating costs low and achieving low raffinate (i.e., product water) Cr(VI) levels. Figure 1 illustrates an A-LIX^{TM} extraction/stripping process. The extraction and stripping reactions are noted below the figure.

The Cr(VI)-contaminated feed water is introduced into the bottom of the first mixer (Tank 1), 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 mg/L.

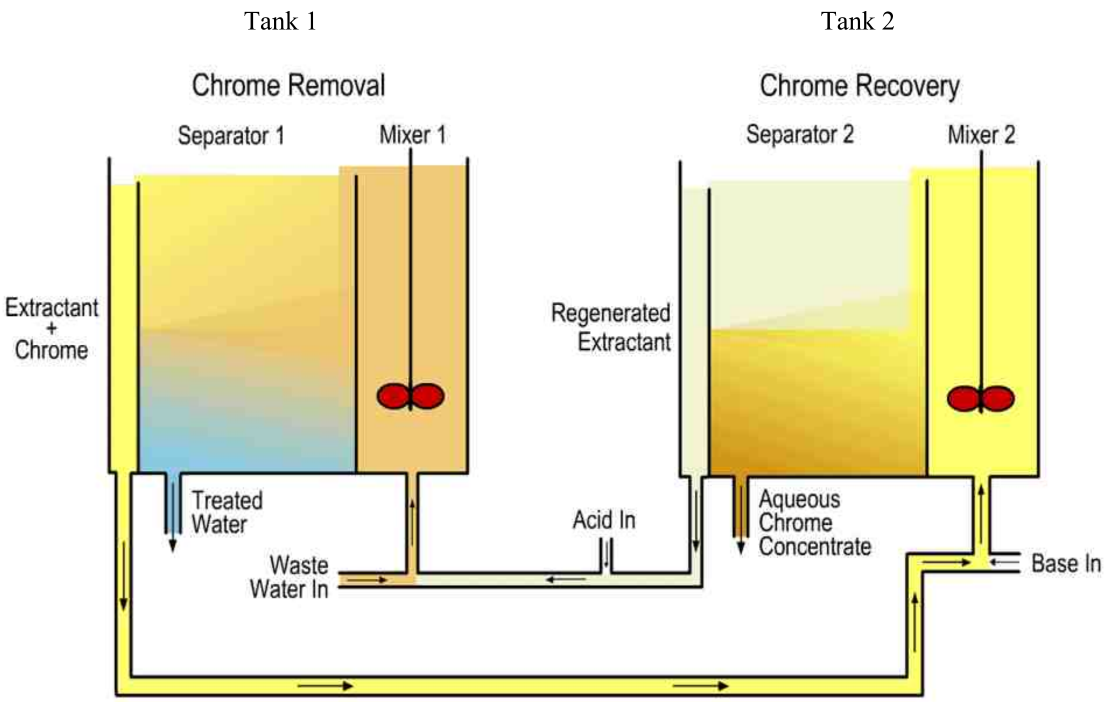

Figure 1: A-LIX^{TM} Extraction/Stripping Process

Extraction: $R_3N + H^+ + HCrO_4^- \rightarrow R_3NH^+HCrO_4^-$
Regeneration: $R_3NH^+HCrO_4^- + 2NaOH \rightarrow 2H_2O + Na_2CrO_4 + R_3N$

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 (Tank 2). In the stripper, sodium hydroxide (NaOH) is added to react with the salt to neutralize 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. The aqueous Cr concentrate is withdrawn from the bottom of the stripper settling-chamber for reuse or recycle.

The key process control parameters, which affect acceptability of the A-LIX^{TM} technology, are noted below:

- Operability and reliability: As staffing at surface finishing shops and industrial wastewater treatment plants (IWTPs) are limited, the need for operator intervention is minimized.

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- Control: For pH control, individual controllers are used to automatically deliver sulfuric acid to the extractors and sodium hydroxide is added to the strippers. Water is added to the strippers for water balance.
- Extractant losses: Extractant make-up rate is an important economic consideration. An oil/water (O/W) separator is used to minimize releases of organic compounds (from the extractant, diluent, and modifier).
- Concentrate value: The Cr(VI) concentrate needs to achieve as high a Cr(VI) level as possible to facilitate economic recycle and/or reused.

A-LIX^{TM} PROCESS DEMONSTRATIONS AND RESULTS

The A-LIX^{TM} development and commercial testing unit was used to process over 1.5 million L of plating shop rinse water from Watervliet Army Arsenal (WAA) and Robins AFB plating shops[5]. The A-LIX^{TM} demonstration unit, see Figure 2, achieved over 99% extraction efficiency during validation testing in a 38,000 L/day (10,000 gpd) scale unit employing automated chemical addition and closed-loop extractant regeneration. Concentrated Cr(VI) was sent for recycle into a steel mill.

Figure 2. Robins AFB Demonstration Unit

Installation and start up of the DoD prototype 114 L/min (30 gpm) or 164,000 L/day (43,000 gpd) capacity A-LIX^{TM} unit began in January 2004 and will continue through April 2004. Views of the facility during construction are shown in Figures 3 and 4.

Figure 3. A-LIX^{TM} Cr(VI) Extraction Prototype Plant

Figure 4. Mixer/Settler in A-LIX^{TM} Prototype Plant

A view of the plant as installed in the basement of the DoD facility's plating shop is shown in Figure 5.

Figure 5. A-LIX^{TM} Prototype Plant installed at the DoD facility

Rinsewater flow rate generation from the plating so far is lower than the 114 L/min design and the plant has been operated at 68 L/min (18 gpm). Through 31 March 2004, 1.5 million L (400,000 gal) have been processed with an average removal rate exceeding 99%. The longest uninterrupted test during the startup period has processed ~700,000 L (180,000 gal). Typical results of the A-LIX^{TM} prototype plant are shown in Figure 6.

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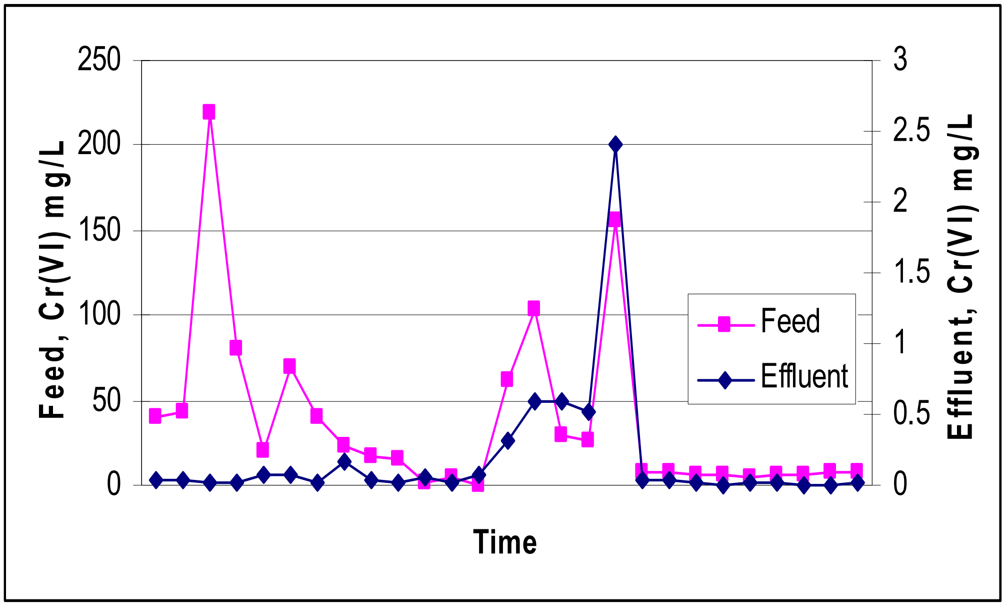

Figure 6. Cr(VI) Versus Time (30 day Period)

As noted in Figure 6, excellent Cr(VI) removal was achieved even with variable levels in the Cr(VI) feed water (1 to 219 mg/L). Over the final 7 days, steady operation was clearly illustrated. Average feed and effluent Cr(VI) concentrations were 37 and 0.19 mg/L, respectively for a 99.5% removal rate.

Figure 7 is a photo of the Cr concentrate product, feed and effluent.

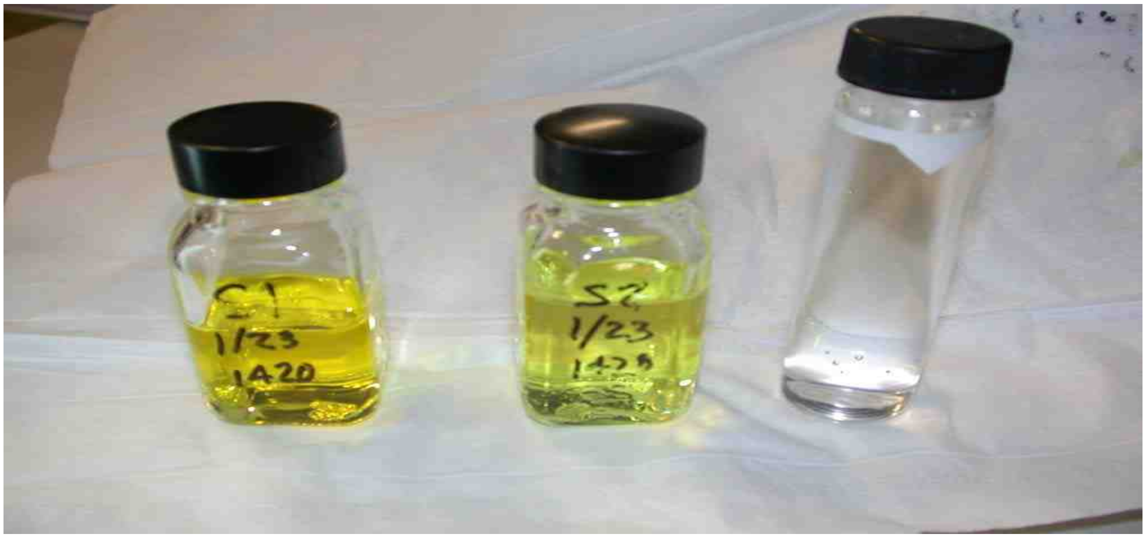

Figure 7. A-LIX^{TM} Concentrate, Feed, and Effluent from DoD Prototype Plant

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PROJECTED A-LIX^{TM} PERFORMANCE

An A-LIX^{TM} system can be designed for multiple extraction stages and stripping stages. To predict the unit performance, the A-LIX^{TM} database was modeled based on equilibrium-stage calculations. The average feed water Cr(VI) concentration of all the demonstration tests conducted at Robins Air Force Base (RAFB) was 55 mg/L. 99.1% removal (outlet minus feed concentration divided by feed concentration) was achieved in practice versus 99.8% predicted. The testing results show that the actual stage efficiency was about 90%, which is typical for mixer-settler extractors.

The actual vs. predicted performance with 90% stage efficiency shows good agreement: stage 1 (1.2 actual vs. 6.7 mg/L predicted), stage 2 (0.3 vs. 1.5), stage 3 (0.1 vs. 0.3), and stage 4 (0.07 vs. 0.05).

COMPARISON TO CONVENTIONAL TREATMENT PROCESSES

The conventional treatment to control Cr discharge includes Cr(VI) reduction to the Cr(III) trivalent form with a reductant such as sodium sulfite, sodium meta bisulfite, ferrous sulfate, or sulfur dioxide under acidic conditions followed by precipitation under basic conditions, settling, flocculation, thickening, dewatering, and disposal of the resultant sludge in a hazardous waste landfill. This produces large amounts of metal-hydroxide sludge. Disposal of this type of hazardous waste can cost over $500/dry ton, and poses a continuing environmental liability. A-LIX^{TM} offers a way to avoid disposal by creating a concentrated Cr(VI) solution for recovery and recycle.

COMPARISON TO ION EXCHANGE PROCESSES

Another common treatment process for Cr(VI) removal is using anionic exchange resins. The wastewater passes through a pressurized treatment tank containing the anionic resin. The anions in the wastewater are ion-paired and adsorbed on the anionic resins. Upon reaching its saturation point, the resin is regenerated using sodium hydroxide. These systems have been in the commercial use for many years. Such a system allows the Cr to be extracted and concentrated. Unfortunately, most resins are non-specific for Cr, and thus remove significant amounts of other anions, such as sulfate, normally present in the wastewater matrix. This process, while effective, is considered very expensive, due to the large up-front capital cost for the equipment and the exchange resins. The spent regeneration brine also creates a difficult and costly disposal issue.

The major difference between the anionic resin and the A-LIX system is in the volume and concentration of the Cr reject streams. The ion-exchange resin systems produces a totally Cr free effluent until regeneration is required. Then a high volume and low concentration reject stream is produced over a few hours (e.g., 38,000 L with a 25 mg/L at the DoD facility); this stream is too dilute to have a recycle value – in fact it represents another significant wastewater stream. So, ion exchange does not eliminate the need for a subsequent treatment step. This is in contrast with the A-LIX^{TM} system which constantly produces a low volume, high concentration (40 L/day with 20,000 mg/L) stream suitable for recycle. Compared to A-LIX^{TM}, the ion exchange resin process is much more costly, uses significantly more chemicals and produces hazardous wastewater requiring additional treatment. The Cr in this wastewater will ultimately be transferred to a hazardous sludge rather than a recyclable product.

ECONOMIC ASSESSMENT

Past economic analysis[5,6] was based on the concentrations of the feed to a 20,000 mg/L Cr(VI) level before sending to the recycler. Payback periods of between 0.9 and 3.9 years were estimated for three military depots. The economic model incorporated capital and operating costs of the A-LIX^{TM} process and credits for decreased wastewater treatment operations, which are principally reduced labor, chemicals and disposal costs.

The economic analysis provides the basis for evaluating the feasibility of treatment options for various Cr(VI) streams typically found in a plating operation, e.g., concentrated spent baths and dilute rinse waters.

Through independent internal water conservation efforts, the DoD facility reduced the volume of spend bath dumps, reduced rinse water volume, and eliminated chromic acid anodize-stripping operations reducing the Cr-contaminated water treatment costs. Data from actual plant construction and initial operation indicate A-LIX^{TM} capital costs and operating costs are slightly lower than originally estimated. During the initial evaluation, significant savings were projected at the industrial waste treatment plant (IWTP) from reductions in (1) chemical usage, (2) sludge handling and sludge disposal, and (3) operating labor. This resulted in a payback period of less than one year.[7]

Many changes in the operation of this DoD facility and its IWTP are under way. For instance, several Cr producing operations have been eliminated. Also, the IWTP staff were realigned and the number of operators reduced. Therefore the magnitude of the earlier projected savings may need to be reduced. A more complete assessment is underway to document savings from chemical usage reduction, water recovery, and reduced sludge generation and disposal costs.

SUMMARY AND CONCLUSIONS

A-LIX^{TM} offers an attractive alternative to conventional wastewater treatment for Cr(VI), due to selectivity for Cr, the ability to be staged for high removal efficiencies, the production of low effluent Cr concentrations, production of a recoverable Cr product, and cost-effectiveness. The process has been highly automated so labor requirements, once fully implemented, are anticipated to be minimal. The process is robust and can handle a range of inlet rinsewater Cr(VI) concentrations. The extractant materials are also regenerated within the processes, so the chemical consumption and costs are minimized.

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