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EXPERIENCES WITH TREATMENT OF MIXED WASTE

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ABSTRACT

Results of a treatability study of chosen mixed wastes from Los Alamos Mixed Waste Inventory are presented. Using electrochemical methods cyanide and heavy metals bearing wastes were treated to below disposal limits.

INTRODUCTION

During its many years of research activities involving toxic chemicals and radioactive materials, Los Alamos National Laboratory (Los Alamos) has generated considerable amounts of waste. Much of this waste includes chemically hazardous components and radioisotopes. The nature of this waste is very diversified; the mixed-waste storage at Los Alamos contains small volumes of a great variety of discarded hazardous and radioactive materials. Knowledge of the contents of waste containers is limited and sometimes unreliable. Continuing to store this waste represents a hazard and is not in compliance with the law. The waste needs to be treated and disposed of. Such treatment must convert the hazardous components of various waste items into nonhazardous forms. Then the waste may be disposed of according to appropriate regulations.

Capital equipment costs are an overwhelming factor when designing a treatment process for a small volume of waste. The amount of capital expense is divided by a low-waste volume. The result is a very high dollar number per unit of treated waste. Because of the diversity but rather small volumes of the wastes at Los Alamos and other re-search and development institutions, it is economically advantageous to develop one versatile process that can treat different kinds of waste.

ELECTROLYTIC APPROACH TO WASTE TREATMENT

We chose to use an electrochemical process for the treatment of many mixed waste components. The electro-chemical process, which we are developing, can treat a great variety of waste using one type of equipment built at a moderate expense. Such a process can extract heavy metals, destroy cyanides, dissolve contamination from sur-faces, oxidize toxic organic compounds, separate salts into acids and bases, and reduce the nitrates. All this can be accomplished using the equipment and one crew of trained operating personnel.

Such equipment consists of several electrochemical cells. Each cell is designed to electrolyze a separate group of waste. The cells are assisted by a common current recti-fier, a gas-handling system, tanks and piping, and a control system.

Electrochemical processing has other advantages in addition to its ability to treat diversified waste. It has the ability to recover and recycle waste components rather than immobilize and dispose of them. For example metals can be plated on cathodes and recovered or salts can be split into acids and bases and reused.

In most instances the electrochemical processing does not require the addition of chemical reagents—the reac-

tions are driven by the electric current. If there is a secondary waste product it would be another form of the initial hazardous waste component converted to a benign form (without gaining the weight of an added chemical reagent). In many cases the hazardous components are converted to benign gases, such as carbon dioxide or nitrogen, and can be released to the atmosphere without additional disposal costs.

Among the many challenges facing the designers and operators of waste treatment technologies is confronting public opinion. Processes that suffer from adverse public perception have little chance of success. Electrochemical treatments operate at low temperature and ambient pressure. Great control can be exercised over the reactions via the application of applied potential or current so there is little chance for a runaway reaction or explosion. In many cases the reaction can be instantaneously terminated by simply turning off the power supply. For these reasons electrochemical waste processing is remarkably prone for positive public perception.

The electrochemical apparatus is easily scaleable. Single-cell modules are simply combined much like building bricks to deliver any desired output. Each of them operates independently. The risk of scale-up problems and possible failures, quite often experienced by the chemical industry, are thus alleviated. Finally, the cost of setting up and operating an electrochemical treatment is relatively inexpensive.

SURROGATE WASTE TESTS

We developed experimental methods and conditions for treatment of toxic metals, cyanides, and some organic compounds. We used surrogate waste compositions. During these tests our waste compositions were well defined, we dealt with pure solutions, and we had the comfort of not having radioactivity in our systems. Some of this experimental work has been presented at The Seventh Special Symposium - Emerging Technologies in Hazardous Waste Management[1] held in Atlanta, Georgia in 1995. In these experiments the conditions were found for electrochemical treatment of waste containing cadmium, mercury, chromium, copper, cyanides, and some organic compounds. Results included the following:

- We found that cadmium can be effectively removed from solutions using the RETEC cell with aluminum cathodes, DSA anodes, and polyacrylamide as depolarizer. A chlorine scrubber should be considered when treating cadmium chloride solution.
- Copper stripping can be performed in a cell with graphite bead packed-bed cathodes and DSA anodes separated by ion exchange membranes. No depolarizer is required.

- Mercury may be easily removed from its inorganic soluble compounds by electrolysis using graphite cathodes and DSA anodes in the RETEC cell.
- Free and complex cyanide can be electrolytically destroyed below disposal limits using graphite cathodes and DSA anodes in an undivided cell.
- The best procedure for electrochemical removal of chromium(VI) is electrolysis in an undivided cell with copper cathodes and carbon steel anodes. Part of the chromium is electrochemically reduced to metal and part remains in the solution as chromium(III). The electrolysis must be followed by alkaline precipitation of chromium hydroxide. Chemical reduction of chromium(VI) by ferrous iron contributes to the electrochemical reactions. The ferrous ions are present in the solution due to anodic dissolution of carbon steel.
- We have also investigated the electrochemical oxidation of selected organics that are known components of mixed wastes. The goal was to oxidize the organic component to carbon dioxide by direct or mediated electron transfer, then recover the heavy metal component for recycling prior to disposal. Mediated oxidation was carried out using cobalt(III) that was generated by oxidation of cobalt(II) at the anode. As anticipated there was a unique set of reaction conditions for each organic compound or class of organic compounds studied. For example in the oxidation of isopropanol at room temperature, with or without a mediator present, the reaction proceeds rapidly with the generation of acetone, the two electron oxidation product. A second two electron oxidation of the acetone produces acetic acid at a rate approximately one order of magnitude slower. The generation of acetic acid is essentially quantitative and the reaction ceases at that point. Further oxidation to carbon dioxide can only be accomplished by continuing the electrolysis at an elevated temperature. For a given organic, as the degree of oxidation increases, the difficulty of further oxidation also increases. Thus one can predict the order of ease of oxidation to be alcohols < aldehydes, ketones < carboxylic acids. Therefore, selected organics can be effectively destroyed by conversion to carbon dioxide using mediated electron transfer oxidizing agents. Each compound or class of compounds will have a unique set of operation parameters that will result in optimum current/destruction efficiency.

Bench-scale tests clearly demonstrated the feasibility of electrochemical systems for treatment of hazardous mixed wastes. For all investigated elements and compounds, the concentration of the hazardous component was decreased below disposal limits. Process conditions for treatment of wastes containing toxic metals, cyanides, and organic compounds have been determined.

Having gained experience and confidence, and having defined the parameters of operation for various waste components, we decided to continue with the optimization in a real life environment. We began the treatability study of mixed waste from Los Alamos Mixed Waste Inventory. We have learned valuable lessons while treating the mixed waste. Some of them are briefly discussed below.

MIXED WASTES TREATABILITY STUDY

A. Equipment and Analytical Set-up.

The generic experimental set-up consisted of the electrolytic cell (RETEC 07), batch tank with mixing, a pump (Cole-Palmer Masterflex 7591-50), and a rectifier (Darrah Electric Comp. R35) or a pulse rectifier (Dynatronix DPR20-100-400). A control set included pH-meters (Orion 250A and Corning pH-meter 340), thermometers or thermocouples, volt- and am- meters, a multichannel chart recorder (Yokogawa LR4110), and a digital coulometer (Electro-synthesis Inc. ESC640). A low pH alarm was used during experiments with cyanides. Concentration of species was measured with an AtomScan-16 ICP spectrometer (Thermo Jarell Ash Corp.).

RETEC 07 is a commercially available cell[2]. It consists of a 12 L rectangular vessel with inlet and outlet ports, flow distributor, and slots for electrode placement. The cell is furnished with 8 Dimensionally Stable Anodes (DSA, titanium grids covered with mixture of titanium oxide and rare earth oxides) and 7 cathodes. The cathode material depended on the composition of waste to be treated. Electrodes are 22.3 x 11.8 cm large.

The composition of electrolyzed solution was determined using anodic stripping voltammetry (Hg), inductively coupled plasma - atomic emission spectroscopy (ICP-AES; Cu, Hg, total Cr), UV-VIS spectroscopy, and potentiometry (cyanide).

Each determination was repeated 3 times for the voltammetric, UV-VIS, and potentiometric measurements. For each element the ICP-AES measurements were performed at two or three various wavelengths and the intensity of light emission was measured 3 or 4 times for each wavelength. Usually the relative standard deviation was less than 2% for the voltammetric and spectroscopic measurements and less than 5% for potentiometric measurements. When the standard deviation was greater than 5% - the value was rejected and the whole experiment repeated.

Free cyanide concentration measurements were done with a cyanide ion specific electrode (Orion, model 9606 Combination Cyanide Electrode). The electrode was calibrated immediately before and after each 10-15 determinations. The mean slope of the calibration curve was equal to the theoretical Nernstian value (at 25°C 59 mV for 10-fold change of cyanide concentration). The maximum devia-

tions which occurred during several weeks of measurements were less than ±2 mV.

Total cyanide analysis was performed according to standard method[3,4] SW846-9010. In this method a cyanide bearing sample is acidified with 50% H_2SO_4 and heated. The liberated gaseous HCN is next absorbed in a NaOH solution. Because of the absence of complexing cations in the NaOH solution, the free cyanide concentration is equal to total CN⁻ concentration. The concentration of absorbed CN⁻ was measured using the Cyanide Combination Electrode or an Automated Cyanide Analyzer (AP1214, Leeman Labs, Inc.). In the AP1214 a sample is mixed with chloramine T, pyridine, barbituric acid, and phosphate buffer, and a resulting colored compound is determined spectrophotometrically at 575 nm. The differences between potentiometric and spectrophotometric measurements were less than 3% (7% for CN⁻ concentrations less than 1 ppm).

For Cr(VI) determination the sample pH was adjusted to about 12 and an absorption peak for CrO_4^{2-} anion was measured[5] at 366 nm using a HP 8452 diode array spectrometer. Total chromium concentration was measured either by ICP-AES or by UV-VIS spectrometry after oxidation of Cr(III) to Cr(VI) by H_2O_2 in alkaline media. Cr(III) concentration was calculated as a difference between total chromium and Cr(VI) concentrations.

Gas chromatography (Hewlett-Packard 5890 GC) and gas chromatography /mass spectrometry (Hewlett-Packard 970 MS) were used to analyze the organics.

All solutions were made using deionized water and reagent grade chemicals.

Electrolyses were conducted with constant or pulsating current. All direct current experiments were performed in current control mode. If continuous monitoring of concentration changes was impossible, small samples of solution were taken every 15 to 30 minutes depending on the predicted total electrolysis time. During electrolysis of inorganics, solutions were neither heated nor cooled (except heating by the current flow through the solution). Except for some chromium electrolyses the temperature did not exceed 42°C. Several chromium electrolyses employed very large currents. In these cases the solution temperature rose to about 70°C due to the ohmic heating.

Post-treatment solutions (except solutions resulted from cyanide destruction) were disposed to the Radioactive Liquid Waste Treatment Plant. All of them met disposal criteria (below 5 ppm of Ag and Cr). Cyanides are a listed waste. Every waste resulted from treatment of cyanide bearing waste is considered by definition as a hazardous waste and had to be properly disposed in a hazardous waste permitted landfill.

B. Mixed Wastes Selected For The Study.

Several mixed waste items were selected from LANL mixed waste inventory. Description and amounts of wastes

are presented in Table 1. Except for "Ag plating bath" and KCN all waste containers were found in a good condition. Wet, solid "Ag plating bath" was placed in a broken beaker with a slightly corroded lead frame. The beaker was wrapped in a plastic bag. Part of the waste leaked out and contaminated sawdust packing material. KCN was placed in a glass bottle with full of holes cap (like a salt shaker). The bottle was wrapped with paper towels and placed into metal can. Other (sawdust) and inner (towels) packing materials were found wet and the can was very corroded. Cyanides were found present only in the inner packing material. Contaminated packing materials were leached 3 times with diluted NaCN solution and finally with water. The rinsing waters were analyzed for presence of cyanide. When the concentration of cyanide was less than 1 ppm the rinsing was terminated. Solutions resulting from leaching procedures were employed to dissolve the main volume of this waste.

Table 1. Mixed Wastes Used in the Treatability Study

Description	Quantity
CuCN unused chemical	0.45 kg
Ag plating bath (with cyanide)	0.9 kg
Cu plating bath (with cyanide)	2-10g
potassium cyanide	1.0 kg
mercurous nitrate	0.5 kg
mercuric nitrate	0.5 kg
chromium(VI) in solution	2.0 L
used chromic acid	17.5 L

Although most all solids were found in a good condition, their appearance and properties had changed. KCN and mercury compound were slightly colored (fresh salts are colorless). Small sample of CuCN dissolved in NaCN solution resulting in a dark mixture. Removing the items from bottles and dissolution of solids was always somewhat problematic.

C. Treatment Methods.

1. Cuprous cyanide. Solid CuCN was dissolved in basic solution of NaCN. The bottles containing both wastes: "unused chemical" and "Cu plating bath" were rinsed with a small amount of NaCN solution and deionized water. The rinses were added to the treated solution. This solution contained 0.29 M (18.4 g/L) total Cu, 0.07 M free CN^-, 1.17 M (30.4 g/L) total CN^-, it had the pH=13, and volume 10.0L. The solution was electrolyzed in a RETEC 07 cell with copper mesh cathodes and DSA anodes. A 30 A constant current was used. Voltage changed within range 2.8 V to 4.2 V. The pH was dropping during the electrolysis. To avoid HCN gas evolution 50% NaOH was added in 3 portions. The total NaOH use was 135 ml. After 23 hours of the electrolysis the total concentrations were reduced to $2.3 \cdot 10^{-5}$ M (0.60 ppm) for CN^- and

$7.9 \cdot 10^{-7}$ M Cu (50 ppb). Overall current efficiencies were equal to 88.2% for anodic reaction ($CN^- + 2OH^- - 2e \rightarrow CNO^- + H_2O$) and 11.0% for cathodic reaction ($Cu(CN)_4^{3-} + e \rightarrow Cu + 4 CN^-$). The course of electrolysis is illustrated in Figure 1.
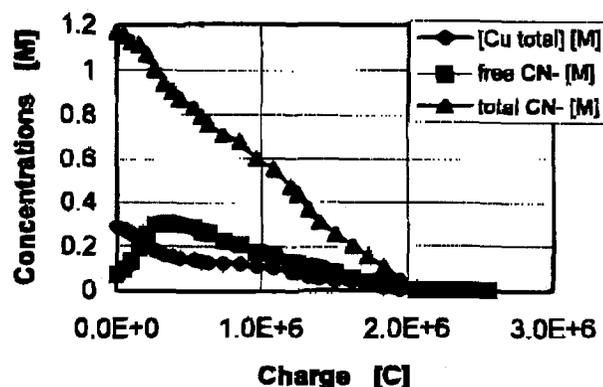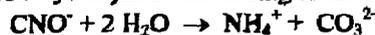

Fig. 1 The course of CuCN waste electrolysis. Values of total CN^- concentrations were calculated based on concentrations of free CN^-, total Cu and literature[6] stability constants for $Cu^+ + CN^-$ complexes.

The post-electrolysis solution was neutralized with conc. H_2SO_4 and evaporated. 1070 g of Na_2SO_4 was obtained as a final product (from Na^+ balance 1072 g should have been obtained).

2. Ag plating bath. This solid waste wasn't homogeneous. Some of the crystals were greenish, the others were colorless. Silver contents ranged from 8.6 to 36.0% in different samples. The average Ag content was 26.4% (w/w). The other main components averaged: 32.4% of K, 4.2% of Na and 13.9% of CN^-. In addition to Ag, small amounts of other metals were found: Cd 0.007%, Cr - 0.011%, 0.03% Cu. Ba, Pb, and Hg were absent. Cl^- and CO_3^{2-} anions were present in this waste but only qualitative analyses were performed.

The whole amount of waste was dissolved in water, resulting in 11.0L of solution containing 0.20 M (21.6 g/L) of total Ag and 0.44 M (11.4 g/L) of total CN^-. The concentration of free CN^- was equal to 0.016 M and the pHwas equal to 11.0. This solution was electrolyzed. After several minutes of electrolysis it became yellow and kept darkening to a light brown color. This trend was reversed after six hours of the electrolysis when the color began to lighten to finally become light yellow. The presence of ammonia was detected over the solution. A literature study revealed[7,8] that at high CN^- concentration CN^- radicals formed at the anode tend to polymerize with hydronium ion to form azulmine, a yellow to brown colored polymer of HCN. Formation of azulmine depends on the CN^-/OH^- ratio[9]. During our experiments when the initial CN^-/OH^- ratio

was high, the solution became light yellow a few minutes into the electrolysis indicating polymer formation. The solution gradually darkened with time. However, after a couple of hours when the CN⁻/OH⁻ ratio dropped, the solution began to clear. At the completion of the electrolysis, only carbonate, chloride, and ammonia were identified in the solution. Most likely the cyanate ions formed during the electrolysis hydrolyzed[10] according to the reaction:

$$CNO^- + 2\,H_2O \rightarrow NH_4^+ + CO_3^{2-}$$

The pH of the solution was decreasing during the electrolysis. Caustic was being added to maintain the high pH. Totally 135 ml of 50% NaOH was added. After 15 h 50 min. of the electrolysis the volume of the solution dropped to 9.8L and the concentrations decreased to: total Ag $9.3 \cdot 10^{-6}$ M (1.0 ppm); total CN⁻ $3.4 \cdot 10^{-5}$ M (0.90 ppm), free CN⁻ $1.5 \cdot 10^{-5}$ M (0.39 ppm), pH=10.3. The course of the electrolysis is shown in Figure 2.
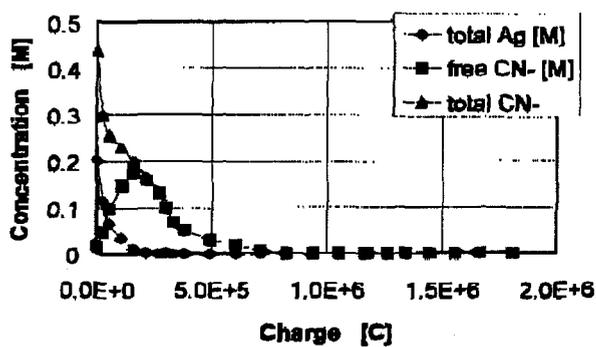

Fig. 2 The course of "Ag plating bath" waste electrolysis. Values of total CN⁻ concentrations were calculated based on concentrations of free CN⁻, total Ag and literature[6] stability constants for Ag⁺ + CN⁻ complexes.

After electrolysis solution was acidified to pH~5 and evaporated to 5.0 L. During these operations color of the solution changed from light yellow to very light green (probably after pH decrease yellow Cr(VI) was reduced to green Cr(III). By AES-ICP 24.5 ppm of total Cr was found in the solution (for chromium disposal limit is 5 ppm). In order to remove chromium, the solution was further acidified to pH=2 and 5 g of FeCl₃ were added. After neutralization to pH=7 the solution was left overnight for Fe(OH)₃ and Cr(OH)₃ sedimentation. Next day a clear solution was decanted. The total of 3.5 g of Fe(OH)₃ and Cr(OH)₃ containing precipitate was collected and added to another chromium containing waste from this treatability study. The decanted solution contained 1.1 ppm of Cr and 0.13 ppm of CN⁻. Finally the solution was evaporated and the obtained solid dried at 140°C. 1100 g of K₂SO₄ + Na₂SO₄ mixture remained. 55.5 g of almost pure metallic silver was very easily scrapped from graphite cathodes. The rest of silver (185 g) firmly stuck to the graphite and was removed using hard scrapping. Total 240.5 g of silver was recov-

ered. From material balances 472 g of Na₂SO₄ and 632 g of K₂SO₄ (total 1104 g), and 238 g of Ag should have been obtained.

3. Potassium Cyanide. The blackish solid was dissolved in a NaOH solution and electrolyzed using copper mesh cathodes and DSA anodes. The initial solution had 5.0L volume, pH=13.3, and contained 1.43 M (37.2 g/l.) of CN⁻. Its color was dark brown. Constant 20 A current was applied. Voltage changed from 2.8 to 3.6 V. These changes could be related to the pH and conductivity changes: when pH dropped - voltage increased due to increase of ohmic resistivity of the solution; when NaOH was added to increase the pH - voltage decreased. During the electrolysis, the initial dark color of the solution slowly disappeared. After 23 h 30 min. total CN⁻ concentration dropped to $5.4 \cdot 10^{-6}$ M (0.14 ppm) and the current source was disconnected.

Following the electrolysis the solution was acidified to pH~6 with concentrated H₂SO₄. During this operation a large quantity of CO₂ evolved. A sample of the final solution was analyzed by AES-ICP for presence of RCRA metals (Ba, Ag, Cd, Cr, Hg, Pb) - none of them was found. Only small amounts of copper were found (~1.5 ppm, probably from dissolution of copper cathodes). At the end the solution was evaporated and 635 g of solid (K₂SO₄ + Na₂SO₄) was obtained. From Na⁺ and K⁺ balances 94 g of Na₂SO₄ and 542 g of K₂SO₄ (634 g total) should have been obtained.

4. Mercury nitrates. Hg₂(NO₃)₂ is a white solid. The compound found in the waste bottle was slightly yellowish. The whole amount of solid was placed in a large Erlenmeyer flask and ~8 L of water was added. The pH was adjusted to pH=2 with concentrated HNO₃. This mixture was stirred overnight. A small amount of solid remained undissolved. The cloudy solution was filtered under vacuum. Tiny specs of yellow and red residue were collected on the filter paper. Both kinds of solids easily dissolved in concentrated HNO₃ (without any fumes of NOₓ); the solution was combined with the main solution in the large flask. Probably yellow and red solids were two polimorfic forms of HgO. If there were Hg(0) or Hg(I) present in precipitate - during dissolution in HNO₃ some brown fumes of NO₂ would have been visible. Water was next added to the main solution to the total volume of 10.0 L. This solution was placed in a RETEC cell and electrolyzed. The course of electrolysis is illustrated in Figure 3.
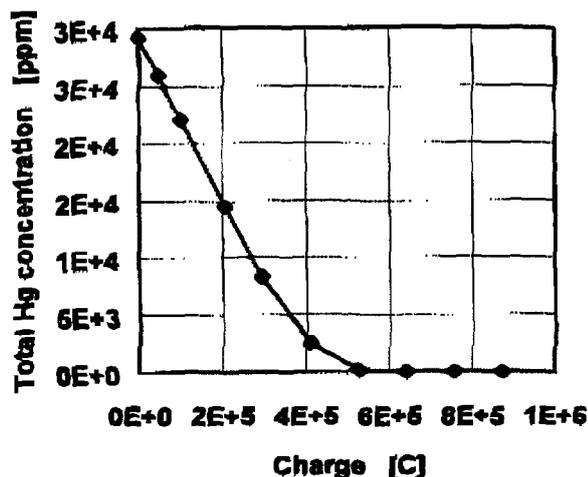
Fig. 3. The course of $Hg_2(NO_3)_2$ electrolysis. Conditions: 7 graphite cathodes; 8 DSA anodes; current 30 A, voltage 2.0 - 3.6 (voltage was increasing during electrolysis). Initial volume 10.0 L; total Hg conc. 29.2 g/L; initial pH 1.20. Total time of electrolysis 17 h 10 min. Final conditions: volume 9.3 L, total Hg concentration 1.0 ppm. Overall current efficiency: 16.2%

After the electrolysis 293.5 g of liquid mercury was collected on the bottom of the cell in a form of small drops contaminated with graphite dust. The after-electrolysis solution was decanted from the cell to an Erlenmeyer flask. Liquid mercury was placed in a large beaker and rinsed by decantation several times with DI water. All rinse water was added to the after-electrolysis solution. This solution was next used to dissolve mercuric nitrate which was the next waste item.

$Hg(NO_3)_2$ is a white solid. Compound in the bottle was a little yellowish. The whole amount of solid was placed in a large Erlenmeyer flask and 9.8 L of after-electrolysis solution from $Hg_2(NO_3)_2$ treatment was added. This mixture was stirred overnight. Small amount of solid remained undissolved. The cloudy solution was filtered under vacuum and filtrate was collected. A small amount of black residue was collected on the filter paper. This residue didn't dissolve in concentrated HNO_3.

The filtrate was diluted to 10.0 L, placed in a RETEC cell and electrolyzed. Conditions and the course of the process were similar to those for $Hg_2(NO_3)_2$. The concentration of Hg was decreased from 33.1 g/L to 1.3 ppm. During 13 h. of the electrolysis 329 g of liquid mercury was recovered. Overall current efficiency was equal to 7.5%.

The after-electrolysis solution was decanted from the cell to the Erlenmeyer flask and few drops 30% H_2O_2 were added to oxidize mercury ions to $Hg(II)$. Next day a small amount of saturated Na_2S solution was added. Due to pre-

cipitation of HgS total concentration of Hg in solution dropped below ICP-AES detection limit. Because of HgS passes the TCLP test - it could be disposed of as a non-hazardous waste.

5. Chromium wastes. There were no "synthetic waste" with similar composition treated previously so different methods were tested.

Direct current electrolysis was the first among the electrochemical methods to be tested. 10 L of the solution was electrolyzed in a RETEC cell with 8 graphite anodes, stainless steel cathodes (sizes and number of cathodes were varied). Cathodic current density was changed from 2.2 A/cm^2 to 0.04 A/cm^2 (by changing overall current and cathode surface area). At no current density chromium was deposited.

Pulse current electrolysis was tested next. During 4 hours of electrolysis a bright layer of chromium was deposited on stainless steel cathode (it looked like a mirror). The ICP measurements showed that only initially concentration of Cr dropped from 0.67M to about 0.66M. During the last 3 hours of electrolysis total Cr concentration remained constants.

Direct current electrolysis with amalgamated cathode was also tested. During the first hour of electrolysis total chromium concentration dropped very slightly (from 0.67M to about 0.66M) and remained constants during next 4 hours of current flow.

These experiments showed that electrochemical route is not effective for this kind of waste. Chemical methods were pursued next.

Due to the presence of concentrated H_2SO_4 the wastes were very corrosive and had to be neutralized before disposal. This forced a hydroxide precipitation as a chemical method for chromium removal.

First, 50% NaOH was added very slowly to neutralize 85% of the acid. The mixture became hot. After cooling down to 40-50°C some white-greenish precipitate (Na_2SO_4 contaminated by Cr(III)) was filtered out. The precipitate was rinsed several times with water. The rinsing water was added to the filtrate and neutralized to pH~7 (±1). The mixture was left overnight to allow the precipitated $Cr(OH)_3$ to settle down. Next morning, a clear solution was pumped out and green slurry of $Cr(OH)_3$ was moved to a cylinder and left to settle down again. The clear solution was analyzed for presence of chromium. In 3 batches total concentration of chromium (after removing $Cr(OH)_3$) was equal to about 20 ppm due to the presence of Cr(VI) (solutions were slightly yellow). About 2 g of sodium dithionite ($Na_2S_2O_4$) was added to each batch to reduce chromium to Cr(III). The pH was adjusted again to ~7 and the solution was allowed to settle down. Next morning, the total concentration of chromium in the solution collected over $Cr(OH)_3$ precipitate was below 5 ppm. That

met the disposal limit to the radioactive liquid effluent plant.

The greenish Na_2SO_4 precipitate was analyzed for presence of chromium. Eight 1 g samples were dissolved in 100.0 ml of water. Concentrations of chromium varied from 0.17 ppm to 25 ppm necessitating the need to treat this precipitate.

The Na_2SO_4 precipitate obtained earlier during the 85 % acid neutralization was dissolved in water and the pH of the solution was adjusted to 7. Next morning the solution was still cloudy. About 1g/L of $FeCl_3$ was added to coagulate the $Cr(OH)_3$. The pH had to be adjusted to 7 again. Next day, after $Cr(OH)_3 + Fe(OH)_3$ had been settled down, the total chromium concentration in the clear solution decanted from over the precipitate was below 2.0 ppm. This solution was disposed of to the Radioactive Liquid Waste Treatment Plant.

The dense slurries of $Cr(OH)_3 + Fe(OH)_3$ were mixed together, placed in stainless steel trays and dried at 140°C. The total of 4.63 kg of $Cr(OH)_3 + Fe(OH)_3 + Na_2SO_4$ mixture was obtained from all batches.

Small samples of the dry slurry were cemented. Several weight ratios were tried. Low Alkaline Portland Cement 5 was used. After adding water the wet cemented waste was placed as a thin layer in a small aluminum tray and left for 3 days to dry. Next the dry cement forms were crushed and powdered with a mortar. Small samples were taken for the TCLP tests. The results are presented in Table 2. Similar tests were performed with samples of the dry slurry prepared by numerous ways (roasted over small flame, roasted and sintered over large flame, dried at 140°C). Results varied depend on place and appearance of the sample (Samples taken from different places varied in color from almost white to light green or blue-green). Total chromium concentration in these samples was varied from 3.1 to 28.3 ppm. The TCLP limit for Cr land disposal is 5 ppm. Only the cemented waste samples passed this criterion. This indicated a necessity for waste cementation.

Table 2. Results of the TCLP Tests for the Chromium Waste Residues.

Description	TCLP result (total Cr concentration)
dry slurry sample 1 (no cement)	33.6 ppm
dry slurry sample 2 (no cement)	29.4 ppm
dry slurry sample 3 (no cement)	33.9 ppm
5% of dry slurry + 95% cement	0.94 ppm
10% of dry slurry + 90% cement	1.06 ppm
20% of dry slurry + 80% cement	1.63 ppm
50% of dry slurry + 50% cement	2.58 ppm

Based on cementation results in Table 2 the approximate composition of 20% of slurry and 80% of cement was chosen. Every chromium waste residue was cemented. Appropriate amounts of waste and cement were placed into a polyethylene bags with interlocking seals and mixed together. Next water was added and mixed with solids. Open bags were left for a week to dry and harden. After this, two plastic bags were randomly chosen, the cement forms were crushed and small pieces were taken out. Approximately 50 g sample was collected this way and subjected to the TCLP tests. Three tests were performed. The resulting Cr concentrations were 0.97 ppm, 0.90 ppm and 0.95 ppm with the average of 0.94 ppm.

CONCLUSIONS

Valuable lessons were learned during these small scale treatability studies with mixed wastes.

It takes considerable resources to handle and treat the mixed waste. These resources must include: radiation measurement capability, abundant chemical analysis capability, access to plentiful literature, and great knowledge and expertise in various aspects of chemistry, as well environmental regulatory and legal counsel. Only a large scientific organization such as a national research laboratory, or a university, can provide these capabilities. We have drawn from these resources across Los Alamos National Laboratory very extensively.

Major effort must be dedicated to analyzing the waste. In many cases the content of the waste drums is not known or is ill defined. Even if the description is reasonable, some doubt remains. For these reasons opening a drum with waste is a hazardous operation and must be handled with tremendous safety and care.

It is much more difficult to perform the treatment of real waste than it was with the surrogates. Problems occur with the dissolution of some compounds. Some wastes have aged over time, hardened, went through changes in crystalline phases, cross-crystallized or grew to the container walls. Some of the containers may be broken and the hazardous and radioactive compounds might have leaked into drum packing materials (which often are sawdust, plastic, or vermiculite). These materials must be cleaned from waste components. Sometimes it involves long leaching procedures. Appropriate leaching solvents have to be found and utilized. Sometimes analysis of the packing material is necessary. The experience from this treatibility study shows that the initial waste preparation steps may consume up to 50% of the treatment time for low volume items.

Other complications arise from the existence of minute quantities of impurities which may display catalytic activities thereby accelerating or inhibiting reactions. Small amounts of impurities may also force additional steps in treatment as it happened with chromium impurity in the "Ag plating bath" waste.

Another problem is the final waste minimization. Unlike with surrogate solutions, radioactive waste should be handled with minimum use of aids such as solvents, rinse

water, paper, rubber, etc. In the end they all constitute radioactive waste and must be disposed accordingly.

The small amounts of wastes used in this treatability study didn't allow to find optimal conditions for their treatment. Current efficiencies for metals' deposition were not impressive. However no stress was put to increase the current efficiency. It is necessary to perform a set of experiments to find out the best conditions for treatment of a specific kind of waste. The experiments performed with "synthetic waste" are always easier but do not reproduce the composition and complexity of real waste treatment. Hence treatability studies with mixed waste are a very meaningful and important step for defining the methods and optimizing the conditions of the treatment. Small quantity of waste that may be processed and disposed of as a result of such studies represents an additional advantage.

Current efficiencies of electrochemical processes may be much improved by using more sophisticated cell geometry. The simple rectangular tank cell doesn't allow to deposit metals with large efficiencies from diluted solutions. Usually[11] cells with 3-dimensional or moving electrodes (like packed bed or fluidized bed) have much larger rates of metal removal than batch cell with 2-dimensional electrodes. However a RETEC cell has its advantages. They are: possibility to work at high and moderate concentrations, simplicity of cleaning, ease of product extraction from the cell, and versatility of the cell. It suffices to change electrodes to adapt the cell for treatment another kind of waste.

In the future some a combination of electrochemical treatment with RETEC-type cell for high concentrations and a more sophisticated one as a as a finishing step at very low concentrations will be considered. This should shorten the time of treatment and increase the efficiency.

REFERENCES

1. J. Dziewinski, S. Marczak, G. Purdy, W. Smith, J. Taylor, C. Zhou, "Electrochemical Treatment of Waste"; *Proc. Emerging Technologies in Hazardous Waste Management VII*, Atlanta, GA, September 17-20, 1995, p. 610-613, ACS Special Symposium

2. Omnipore, Inc., Sugar Land, TX, *Technical Literature for the RETEC Heavy Metal Recovery System.* March 1987.

3. A.E. Greenberg, L.S. Clesceri, A.E. Eaton, eds. *Standard Methods for Examination of Water and Wastewater.* pp. 4-23 - 4-27, 18th ed., American Public Health Association, Washington DC (1992).

4. *Test Methods for Evaluating Solid Waste (SW-846).* 3rd ed. vol. 1A, ch. 5, pp. 9010-1 - 9010-12, United States Environmental Protection Agency; November 1986

5. Williams W.J. *Handbook of Anion Determination.* pp. 55-56 Butterworths, London, Boston, Sydney, Wellington, Durban, Toronto (1979)

6. M.T. Beck, "Critical Survey of Stability Constants of Cyano Complexes", *Pure & Appl. Chem.* **59**, 1703 (1987)

7. Schmidt H., Meinert H., "Electrolysen von Cyaniden in wäßrigen Lösungen.", *Z. anorg. allgem. Chemie* **293**, 214 (1957)

8. Yosimura S., Katagiri A., Yoshizawa S., "Studies on Anodic Oxidation of Cyanide Ion in Presence of Copper Ion. 5. Reaction Products of Anodic Oxidation of Cyanide Ion in Presence of Copper Ion.", *Nippon Kagaku Kaishi (J. Chem. Soc. Japan)* **1980**, 1327

9. Hwang J-Y., Wang Y-Y., Wan Ch-Ch., "Electrolytic Oxidation of Cuprocyanide Electroplating Waste Waters under Different pH Conditions.", *J. Appl. Electrochem.* **17**, 684 (1987)

10. Lister M.W., "Some Observations on Cyanic Acid and Cyanates", *Can. J. Chem.* **33**, 426 (1955)

11. F.C. Walsh, G.W. Reade, "Electrochemical Techniques for the Treatment of Dilute Metal-Ion Solutions" in C.A.C. Sequeira ed. *Environmental Oriented Electrochemistry,* Amsterdam, London, New York, Tokyo, Elsevier 1994