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Electrochemical Treatment of Mixed and
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ABSTRACT.

Los Alamos National Laboratory (LANL) and The University of New Mexico are jointly developing an electrochemical process for treating hazardous and radioactive wastes. The wastes treatable by the process include toxic metal solutions, cyanide solutions, and various organic wastes that may contain chlorinated organic compounds. The main component of the process is a stack of electrolytic cells with peripheral equipment such as a rectifier, feed system, tanks with feed and treated solutions, and a gas-venting system. During the treatment, toxic metals are deposited on the cathode, cyanides are oxidized on the anode, and organic compounds are anodically oxidized by direct or mediated electrooxidation, depending on their type. Bench scale experimental studies have confirmed the feasibility of applying electrochemical systems to processing of a great variety of hazardous and mixed wastes. The operating parameters have been defined for different waste compositions using surrogate wastes. Mixed wastes are currently treated at bench scale as part of the treatability study.

INTRODUCTION.

According to the Resource Conservation and Recovery Act (RCRA) introduced by the US Congress in 1976 and amended in 1984, 1986 and 1988, every hazardous waste must be treated prior to disposal. A hazardous waste containing low levels of radioactivity is categorized as a mixed waste, and additional regulations apply to the treatment of mixed waste, as well as the RCRA regulations. Considerable volumes of mixed waste exist at facilities operated by the United States Department of Energy. These wastes include spent plating and plating rinse baths containing toxic metals and cyanides, halogenated solvents, aromatic compounds, ions and greases, and solutions high in nitrate concentration.

Many treatment technologies exist for these wastes, but they may have drawbacks. For example, many treatments require additional chemicals which, while removing the hazardous or radioactive component, adds to the total disposal volume. Other treatments, such as incineration, have essentially been regulated out of existence. At Los Alamos National Laboratory we are currently investigating alternative mixed waste treatment processes based on electrochemical technologies.

There are some distinct advantages to electrochemical as compared to more conventional treatment technologies. Because electrochemistry is carried out in aqueous solution, the temperature cannot be greater than approximately 100°C so there is little likelihood for radioactive emissions as compared to the high temperature incineration process. Also, for many of the wastes treated it is not necessary to add

chemical reagents, since all of the work is done by the action of electrons flowing through the solution. Thus, no secondary waste is generated in the treatment process. Greater control can be exercised over the reaction via the application of applied potential or current so there is little chance of runaway reaction or explosion. In many cases the reaction can be instantaneously terminated by simply turning off the power supply. Finally, the cost of setting up and operating an electrochemical treatment is relatively inexpensive.

We chose to take the electrochemical route to treat mixed (hazardous and radioactive) waste at Los Alamos National Laboratory. As a result of the treatment the hazardous component of the waste is destroyed or separated and low level radioactive effluent is disposed to the Radioactive Effluent Treatment Plant. The Plant separates radionuclides and discharges clean water to the environment. Substantial quantities of various mixed waste have been accumulated at the Laboratory as a result of weapons development and other activities. These wastes, being the result of non-routine research, are found in a great diversity, but in low volumes of each type. For such situations a versatile process that can combine processing of different kinds of waste represents the best economical solution. We conducted bench scale experiments using surrogate waste compositions to determine the feasibility and establish the parameters for electrochemical treatment of various kinds of waste. We experimented with toxic metals, cyanides, and toxic organic compounds. This paper describes our experimentation.

EXPERIMENTAL

The generic experimental set-up is shown schematically in Figure 1. It consists of the electrolytic cell, batch tank with mixing, a pump (Cole-Palmer Masterflex 7591-50), and a rectifier (Darrah Electric Comp. R35) or potentiostat/galvanostat (EG&G PAR 273). A control set includes 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 (Electrosynthesis Inc. ESC640). A low pH alarm was used during experiments with cyanides.

Several different cells were operated depending on the nature and scale of the experiment. A commercially available RETEC cell¹ was used for larger scale inorganic experiments. The RETEC cell 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 DSA anodes (titanium grids covered with a mixture of titanium and rare earth oxides). The cathode material depended on the composition of the waste to be treated. Some small scale experiments were performed in a 250 ml batch-type cell. The cell geometry and solution flow pattern was similar to that of the RETEC cell. Bench-scale organic destruction experiments were carried out in a two compartment cell fitted with a Nafion ion exchange membrane cell separator and with a condenser over the anode compartment to prevent the escape of volatile organics.

The compositions of electrolyzed solutions were determined using anodic stripping voltammetry (Hg, Cu, Cd), ICP-AES (Cu, Cd, total Cr), and potentiometry (cyanide, Cu). Free cyanide concentration measurements were done with a cyanide ion specific electrode. Total cyanide concentration was measured using the same electrode or with

an Automated Cyanide Analyzer (AP1214, Leeman Labs, Inc.). The method for sample preparation for total cyanide analysis is detailed in SOW #846 (method 9010) or SOW #788 (method 335.2 CLP-M), approved by the USEPA. For Cr(VI) determination the sample pH was adjusted to about 12 and an absorption peak for CrO_4^{2-} anion was measured at 366 nm² using an 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 GC/MS (Hewlett-Packard 970 MS) were used to analyze the organics.

Fig. 1 Experimental set-up.

RESULTS

Cyanides

There are several possible reactions at the anode and at the cathode that may be occurring under alkaline environment:

Anode:

-0.97 V

Cathode:

When a heavy metal is present, such as copper, silver, or cadmium, it will be released from the complex bond, and reduced according to:

Anode:

Cathode:

The situation is additionally complicated by the hydrolysis of cyanate, and the ability of cyanide to combine with hydronium ions to form a polymeric form called azulmine^{3,4}

The 12 L RETEC cell with DSA anodes and several different cathodes was used for electrochemical destruction of cyanide. The results are presented in Figure 2. We observed that in the initial stage of electrolysis, current efficiencies usually exceeded 100 % (based on the reaction $\text{CN}^- + 2\text{OH}^- - 2\text{e}^- \rightarrow \text{CNO}^- + \text{H}_2\text{O}$), indicating a chemical reaction was taking place in addition to the electrochemical process. A literature study revealed^{3,4} that at high CN^- concentration CN^- radicals formed at the anode tend to polymerize with hydronium ions to form azulmine, a polymer of HCN. Formation of azulmine depends on the CN^-/OH^- ratio. When the initial CN^-/OH^- ratio was higher than 5, the solution became light yellow a few minutes into the electrolysis indicating polymer formation. The solution gradually darkened with time. However, after two hours when the CN^-/OH^- ratio dropped, the solution began to clear. At the completion of the electrolysis, only carbonate and ammonia were identified in the solution. Most likely the cyanate ions formed during the electrolysis hydrolyzed according to the reaction (8).

The same RETEC cell was used for electrolysis of cuprous cyanide. The electrolysis started at a cyanide concentration of 200 ppm and was discontinued when the cyanide concentration dropped to 0.08 ppm. Copper was simultaneously removed to less than 0.03 ppm (Figure 3). During electrolysis, some tiny brownish-black solids were deposited on the bottom and on the walls of the cell. These solids contained about 10-15% cyanide and were partially soluble in 1 M HCl. All solid could be dissolved in concentrated HNO_3 with evolution of NO_x . Cu^{2+} ions were found in both acidic solutions. The mechanism of $\text{Cu}(\text{CN})_n^{1-n}$ oxidation isn't clear. Some authors⁵ postulate oxidation of Cu(I) to Cu(II) with liberation of cyanide ions and precipitation of Cu(OH)_2 . Others⁶ suggest that the main product of anodic oxidation of $\text{Cu}(\text{CN})_n^{1-n}$ is CuO . Hwang, Wang

and Wan⁷ analyzed the reddish-brown precipitate that formed at a platinum anode during destruction of complex cuprous and found a mixture of Cu_2O and CuO . This observation agrees with chemical properties of our precipitate.

Fig. 2 Electrolysis of NaCN solution in a RETEC cell. Initial conditions: 3.0 L, 27 g/L of CN^- , 0.1 M NaOH ; DSA anodes, copper mesh cathodes, constant current 18 A. Total time of electrolysis: 23 h. 15 min.; final total CN^- concentration 0.2 ppm; overall current efficiency 35%

Fig. 3 Electrolysis of $\text{CuCN} + \text{NaCN}$ solution in a RETEC cell. Initial conditions: 5.0 L; 200 ppm Cu^+ (as CuCN), 200 ppm CN^- (as CuCN and NaCN), 0.03 M NaCN ; copper mesh cathodes, DSA anodes. Final total concentration: $[\text{Cu}] < 0.03$ ppm, $[\text{CN}^-] = 0.08$ ppm. Overall current efficiency 1.5%

Chromium

Commercial chromium plating baths typically contain chromium as Cr(VI) in concentrations in the range of 200 g/L. Even at these high concentration levels, chromium deposition is characterized by low current efficiency⁸, usually around 10%.

For a more dilute solution, such as might exist in a chromium containing waste, electrochemical deposition of the chromium would operate at too low an efficiency to be useful.

An alternative approach to chromium removal is to reduce the chromium to the +3 oxidation state followed by precipitation as the insoluble hydroxide. To facilitate this reaction, an iron plate was used as the anode. The iron(II) reacted with chromium (VI) in solution to produce iron(III) and chromium (III). The chromium(VI) concentration was lowered from 570 ppm to 5 ppm at a current efficiency of 72%. Following alkaline precipitation, the residual chromium level was reduced to 0.07 ppm.

Cadmium.

The electroreductive stripping of cadmium from aqueous solution was carried out in the RETEC cell. Typically, 12 L of solution containing 13 g of Cd^{2+} per L was electrolyzed for 5-8 hours. The solutions were prepared using either CdSO_4 , $\text{Cd}(\text{NO}_3)_2$ or CdCl_2 . The initial pH was adjusted to approximately 2 with the appropriate mineral acid. During the electrolysis the pH tended to decrease and was held at a pH of 2 by addition of 5.0 M NaOH. Several combinations of cathode materials (nickel and aluminum sheets) and polarizers (polyacrylamide, bone glue and gelatin) were used. The polarizers were necessary to inhibit the reduction of water to hydrogen gas, thereby increasing the overall current efficiency of the process. The best results were obtained with aluminum cathodes and 60 mg/l of polyacrylamide. The average current efficiency was 88% at the 13 - 2 g/l range, and 46% at the 2 - 0.2 g/l range. The cadmium concentration in the solutions was decreased to 0.05 ppm. The cadmium deposit on the cathode was soft and easily removable from the aluminum surface. Current efficiencies and final Cd^{2+} concentrations were independent of the counterion.

Mercury

A small scale experiment was conducted to test the effectiveness of mercury removal from waste solutions using electrochemical methods. A sheet of copper metal served as the cathode and solid graphite as the anode. The surrogate waste solution, originally 27 ppm mercury (HgCl_2 , pH 2, HNO_3), was reduced to 0.122 ppm mercury following electrolysis. The average current efficiency was predictably low at only 7%, due to the low starting concentration.

A larger scale experiment was conducted using the RETEC cell fitted with DSA anodes and graphite cathodes. Mercury was deposited on graphite, coalesced and fell down to the bottom of the cell. Precautions had to be taken to avoid shorts between anodes and cathodes as a mercury pool collected at the bottom of the cell. The initial Hg concentration of 85.4 g/L in 10 L of the solution ($\text{Hg}_2(\text{NO}_3)_2$, pH 2, HNO_3) was reduced to below 1.3 ppm during 8 hours of electrolysis. The overall current efficiency was 47%. The surface of the mercury collected from the cell was slightly contaminated with graphite dust.

Organic Compounds.

We have also investigated the electrochemical oxidation of selected organics that are known components of mixed wastes. The goal is to oxidize the organic component to carbon dioxide by direct or mediated electron transfer, then recover the heavy metal component for recycle prior to disposal. Mediated oxidation was carried out using cobalt(III) which was generated by oxidation of cobalt(II) at the anode.

As anticipated, there are 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 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. Since the oxidation of organics is carried out in aqueous media where there is an unlimited source of oxygen, large organic molecules can be expected to form carboxylic acid intermediates. Therefore one can also expect to achieve complete conversion to carbon dioxide only at elevated temperatures. In acidic aqueous media, the oxidation of cobalt(II) to cobalt(III) occurs at a more positive potential than the solvent. Thus it can never be generated at 100% current efficient since water will be simultaneously oxidized at any applied potential or current density. Once generated, the cobalt(III) is reasonably stable at room temperature, slowly reacting with water to reduce back to cobalt(II). However, as the temperature is raised, this reaction experiences a rather dramatic rate increase such that cobalt(III) is quite unstable. Thus the electron transfer mediator must be continually generated at fairly high current density so that there is a sufficient steady state concentration available to bring about oxidation of the organic compounds present. Under these conditions the overall current efficiency can be expected to be very low. An exception to this behavior is especially seen in small, one carbon molecules. We have found for example that methanol, chloroform and carbon tetrachloride are all converted to carbon dioxide at room temperature at approximately 100% current efficiency. (see table 1)

Table 1. Organic compounds destroyed by mediated electrooxidation.

Compound	Current Efficiency
iso-Propanol	>90%
Acetone	>90%
Acetic Acid	>90%
Chloroform	>90%
Carbon Tetrachloride	>90%
Cheesecloth	~20%
Ion Exchange Resins	not measured

CONCLUSION.

The bench scale studies have clearly demonstrated the applicability of electrochemical systems for destruction or removal of the hazardous component of mixed waste. The conditions of electrochemical processing found during this study were applied to

treatment of the real mixed waste. This waste is currently treated under a treatability study. The process is undergoing optimization and scale-up.

REFERENCES

1. Omnipore, Inc., Sugar Land, TX, Technical Literature for the RETEC Heavy Metal Recovery System. March 1987.
2. Williams W.J., "Handbook of Anion Determination", Butterworths, London, Boston, Sydney, Wellington, Durban, Toronto 1979
3. Schmidt H., Meinert H.; "Electrolysen von Cyaniden in wässrigen Lösungen"; *Z. anorg. allgem. Chemie*; **293**(1957)214
4. 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
5. Hine F., Yatsuda M., Iida T., Ogata Y.; "On the Oxidation of Cyanide Solutions with Lead Dioxide Coated Anode"; *Electrochim. Acta*; **31**(1986)1389
6. Tan T. C., Teo W. K., Chin D-T.; "Electrochemical destruction of complex cyanide"; *Chem. Eng. Comm.*; **38**(1985)125
7. Hwang J-Y., Wang Y-Y., Wan Ch-Ch.; "Electrolytic oxidation of cuprocyanide electroplating waste waters under different pH conditions."; *J. Appl. Electrochem.*;
8. D. Pletcher; "Industrial Electrochemistry"; London; Chapman and Hall, 1982. p.186