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THE TREATMENT AND ANALYSIS OF
CYANIDE WASTEWATER

D. P. Clark, et al

Thickol Corporation

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February 1975

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Thiokol Corporation

February 1975

Final Report for Period September 1973-December 1974

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AIR FORCE SYSTEMS COMMAND
TYNDALL AIR FORCE BASE
FLORIDA 32401

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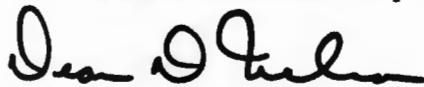
FOREWORD

This report was prepared by Thiokol Corporation, Wasatch Division, Brigham City, Utah, under Contract F08638-74-C-0001. The research was performed under Program Element 64708F, Project 2054.

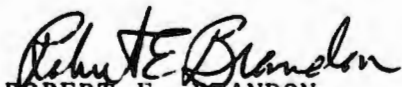
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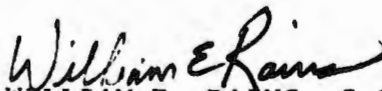
This technical report has been reviewed and is approved.



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ABSTRACT

(Distribution Limitation Statement A)

Electroplating operations and operations involving the case hardening of steel, the neutralizing of acid "pickle scum," the refining of gold and silver ores, and the scrubbing of stack gases from blast and producer gas furnaces produce wastewater streams contaminated with cyanide materials. The Air Force in its routine mission accomplishment generates large volumes of liquid cyanide wastes, a major source of these wastes being their electroplating operations. The necessity of treating these cyanide wastes is established by the Water Quality Act Amendments of 1972. The Thiokol cyanide waste treatment system previously developed under Air Force Contract F29601-72-C-0135 has been optimized in its design and operation to the point where under actual field test conditions at Hill Air Force Base, Ogden, Utah, the cyanide concentration in the discharge of the system never exceeded 0.05 mg/l during a four-week on-line testing program. The system was operated successfully on a daily basis for the four-week period and treated the wastewater overflow from the cadmium plating rinse tanks and stack gas scrubber system. The average concentration of cyanide in the discharge stream was 0.008 mg/l. The average effluent value for cyanate was 5.25 mg/l.

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ABBREVIATIONS AND SYMBOLS

Ag	Silver
AgCl	Silver chloride
AgNO ₃	Silver nitrate
Al	Aluminum
Cd	Cadmium
Cl ₂	Chlorine
Cl ⁻	Chloride ion
ClO ₃ ⁻	Chlorate ion
Cu	Copper
CN (or CN ⁻)	Cyanide (ion)
CNCl	Cyanogen chloride
CNO (or CNO ⁻)	Cyanate (ion)
CO ₂	Carbon dioxide
CO ₃ ⁼	Carbonate ion
Cr	Chromium
Fe	Iron
H ₂	Hydrogen
H ⁺	Hydrogen ion
HCl	Hydrogen chloride (Hydrochloric acid)
HCN	Hydrogen cyanide
H ₂ CO ₃	Carbonic acid
HCO ₃ ⁻	Bicarbonate ion
HOCl	Hypochlorous acid
H ₂ SO ₄	Sulfuric acid
KCN	Potassium cyanide
KI	Potassium iodide
MgCl ₂	Magnesium chloride

ABBREVIATIONS AND SYMBOLS (Cont)

Mn	Manganese
N ₂	Nitrogen
Na ⁺	Sodium ion
NaCl	Sodium chloride
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
Na ₂ SO ₃	Sodium sulfite
NH ₃	Ammonia
(NH ₄) ₂ CO ₃	Ammonium carbonate
Ni	Nickel
OCl (or OCl ⁻)	Hypochlorite (ion)
OH ⁻	Hydroxide ion
Si	Silicon
AFB	Air Force Base
BTU	Energy, British thermal units
e ⁻	Symbol for an electron
ft ³ /hr	Flow rate, cubic feet per hour
gal	Volume, gallon
gpm	Flow rate, gallons per minute
l	Volume, liter
lb/hr	Flow rate, pounds per hour
LEL	Lower explosive limit
mg/l	Concentration, milligrams per liter
ml	Volume, milliliter
ml/min	Flow rate, milliliters per minute
PEPCON	Trademark, Pacific Engineering and Production Company of Nevada

ABBREVIATIONS AND SYMBOLS (Cont)

pH	Measure of acidity
psig	Pressure, pounds per square inch, gauge
RO	Reverse osmosis
scfm	Flow rate, standard cubic feet per minute
TDS	Concentration, total dissolved solids
UEL	Upper explosive limit
UV	Ultraviolet light or energy
µg	Mass, micrograms

SECTION I

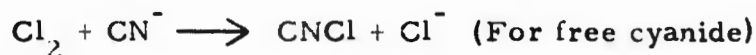
INTRODUCTION

The toxic action of cyanide on living organisms by reducing or eliminating the ability of the organism to utilize oxygen is well known. The action of the cyanides at the acute toxic level is both rapid and fatal. Not only are the cyanides hazardous to animal life but they are toxic to aquatic life as well and can interfere with normal biological processes of natural purification in the streams. The fish in these streams, for example, can be killed either directly by the cyanide, indirectly by the destruction of the organisms on which they feed, or by depletion of oxygen in a stream because of the destruction of the micro-organisms in the water responsible for proper oxygen balance. Even in wastewater the cyanides present a problem since they can impair the biological processes of waste treatment plants, although in low concentrations these processes do reduce the cyanide concentration.

Most of the cyanide wastes which are presently causing stream pollution and are presenting problems in waste treatment plant operation are in the discharge wastes of five industrial processes: metal plating, case hardening of steel, neutralizing of acid "pickle scum," refining of gold and silver ores, and scrubbing of stack gases from blast and producer gas furnaces. The greatest source of cyanide-bearing waste comes from the rinse waters, spillages, and drippings from the electroplating solutions of cadmium, copper, silver, gold, and zinc. It is on the electroplating waste that this project was focused.

The Air Force operates a number of large electroplating facilities in support of their aircraft maintenance program, and from these facilities a significant volume of cyanide contaminated wastewater emerges. A standard procedure for treating these wastes in the past has been what is called the alkaline chlorination process.

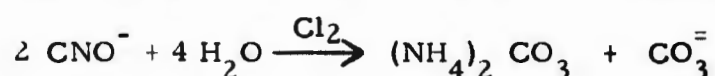
In the alkaline chlorination process, chlorine is injected into the wastewater and the following reactions occur:



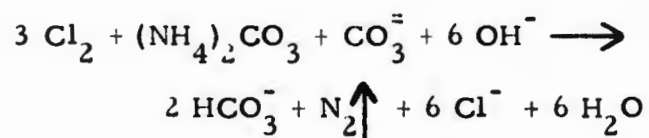
This reaction is practically instantaneous and its rate is independent of pH.



Cyanogen chloride hydrolysis is a fairly strong function of pH. At a pH of 10 to 11, the time for 100% conversion to occur is of the order of 5 to 7 minutes. At a pH of 8.5 to 9, the time is increased to from 10 to 30 minutes.



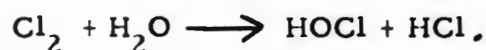
Chlorine does not take part chemically in this reaction step but acts as a catalyst for the reaction.²⁴



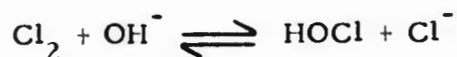
This reaction finally completes the destruction of cyanide to the final products of nitrogen gas and the bicarbonate ion.

If the pH is lowered, the bicarbonate will decompose and liberate CO_2 .

During the addition of chlorine to an aqueous cyanide system the pH drops markedly. To overcome this problem, caustic must be added and is shown taking part in the CNCl reaction as well as in the final reaction where nitrogen is evolved. The pH effect of chlorine hydrolysis is shown as



This is one of the most significant chemical reactions that occur when water and chlorine are brought together. The complete hydrolysis occurs in a few tenths of a second at 65°F. The mechanism of this reaction is thought to be



with the chlorine reacting with the hydroxyl ion rather than with the water molecule itself.

The problems encountered in the operation and maintenance of an alkaline chlorination system such as chlorine **gas leaks**, sensor probe failure, and carbonate scaling, plus the costs of chemical raw materials required by the system make it desirable to develop a new process for the destruction of cyanides in wastewater. In addition, new and more restrictive regulations regarding cyanide discharge are being promulgated. The primary goals of this program were to develop a system for destroying cyanide materials in wastewater which would not be encumbered by the above-mentioned operational problems and would provide treatment levels compatible with the new regulations and at lower operating costs.

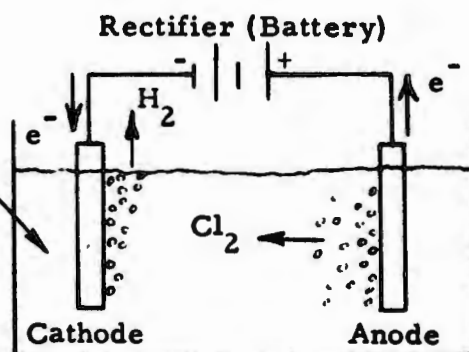
The treatment concept developed and tested during this program is equivalent chemically to that of alkaline chlorination. However, instead of adding chlorine gas directly, the chlorine is generated electrolytically in the wastewater itself. No pH compensation is required because for every equivalent of chlorine that is generated at the anode of the electrolytic cell, an equivalent of hydroxyl ions is liberated at the cathode.

The electrochemistry of the cell is shown by the schematic and cell reactions in Figure 1.

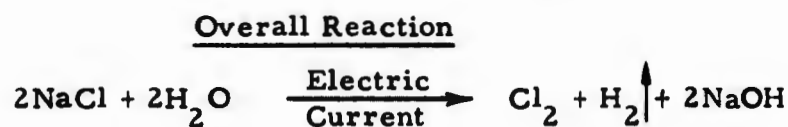
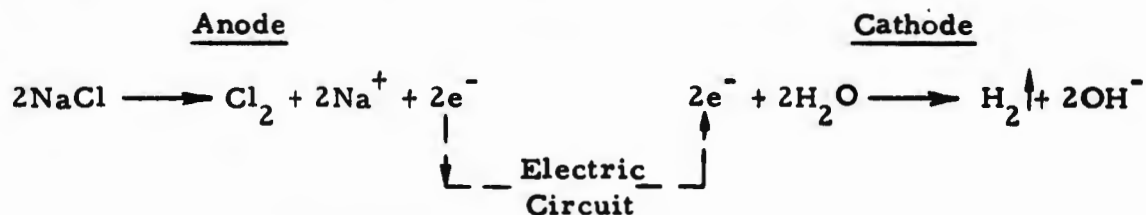
Obviously the same chemical species are present in the system involving the electrolytic generation of chlorine as are present in an alkaline chlorination system. The overall reaction of cyanide destruction

. ELECTROLYTIC CELL

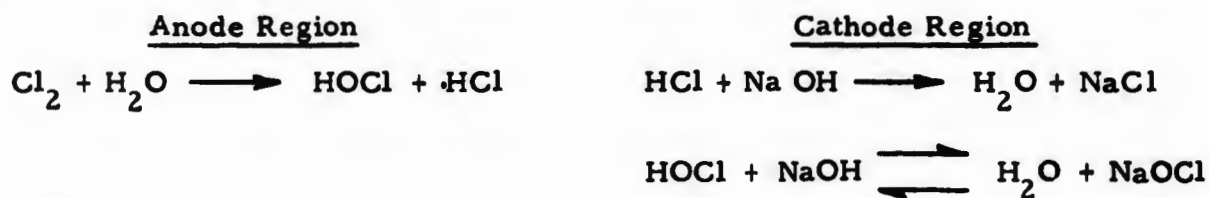
Solution of Salt and
Water (NaCl and H₂O)



. ELECTROCHEMICAL REACTIONS



. CHEMICAL REACTIONS



IN SOLUTION

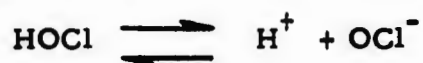
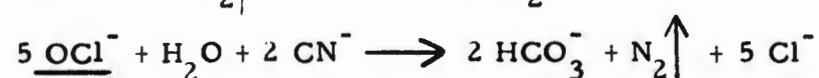
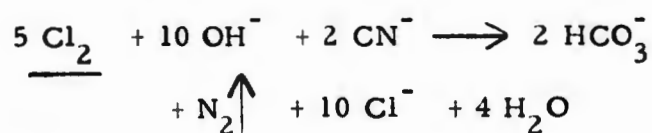
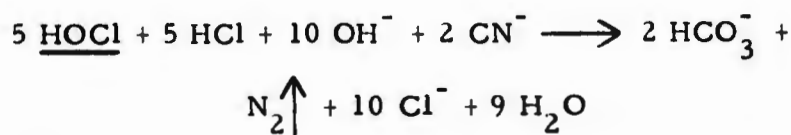


Figure 1. Chlorine Chemistry of Thiokol Waste Treatment System

is the same in both systems and is the same whether one writes it with chlorine as the oxidant or as hypochlorite or hypochlorous acid as the oxidant:



Wastewater from plating facilities contains not only free cyanide (CN^-) but also combined cyanides in the form of heavy-metal complexes. The chlorination of these wastes differs chemically from that of free cyanide in two major ways. First, the complex is more stable to chlorination and reaction times are increased. Second, additional chlorine is required to oxidize certain metals to a higher oxidation state, e.g., cuprous to cupric copper and nickelous to nickelic nickel. Iron as the ferrocyanide complex is easily oxidized to the ferricyanide complex. However, the ferricyanide complex is quite resistant to oxidation by aqueous chlorine.

During the cyanide waste treatment studies conducted earlier, it was discovered that results from cyanide analyses using standard methods could be in error. Indications were that while many treatment processes using chlorination appeared to remove cyanide to non-detectable levels, in actuality, several ppm of cyanide might be passing through the treatment systems and entering the environment. Further work was required to further test the standard procedures and if necessary to modify those procedures to give precise and accurate results in cyanide analyses. In addition, certain improvements were deemed necessary in the destruct system developed under the earlier contract to develop a system capable of preventing the escape of cyanides to the environment.

The cyanide waste treatment program was divided into four main tasks. Task 01 was a laboratory evaluation including a literature review of the methods of analysis for cyanide detection in wastewater and a study of some of the operating variables affecting complete cyanide removal. Under Task 02, System Testing, a cyanide waste treatment system similar to the prototype unit developed under a previous contract was constructed and tested in the Thiokol waste treatment buildings. Task 03, Advanced Cyanide Removal Testing, was designed to provide what might be termed tertiary treatment systems to be added to the basic destruct unit if required. A contract modification was approved by the Air Force, wherein laboratory experimentation with a novel cyanide destruct recycle system was substituted for advanced cyanide removal testing and became the main effort under Task 03. Under Task 04, Field Testing, the cyanide destruct system was palletized and shipped to Hill Air Force Base, Ogden, Utah, for testing in the plating facility there. The system was placed on stream in one of the plating lines and was operated successfully for four weeks processing the overflow liquid from the rinse tanks.

SECTION II

LABORATORY EVALUATION

LITERATURE REVIEW

A review was made of the recent literature to evaluate new methods for treating cyanide waste. Several comprehensive reports were found that discuss the different methods of treatment^{1, 2, 4, 5, 8, 9}. The literature review¹¹ completed previously by Thiokol as part of an earlier program reviewed most of the methods in use at that time. The present literature review was concerned with methods of treatment that could be used with the Thiokol waste treatment system. Examples of these are ion exchange, adsorption, reverse osmosis, integrated treatment systems, and electrolytic decomposition.

ALTERNATE METHODS

Ion Exchange

The ion exchange process for the removal and treatment of cyanide has been evaluated by several parties.^{5, 12, 13} The capacity of any given ion exchange system is dependent upon many variables such as resin type, valence of the complex cyanide,⁵ method of regeneration, and pore size of the resin. Ion exchange of complex metal cyanides is, in reality, a concentration technique, not a waste disposal technique. The metal and/or cyanide ions which concentrate on the ion exchange resin must still be disposed of in some acceptable manner after they are removed during regeneration of the resin.

One of the major difficulties experienced with ion exchange is a phenomenon termed "poisoning," wherein certain ions become very firmly attached to the resin and are removed from the resin only with extreme regeneration techniques.¹²

If these foreign ions are not removed, the number of active exchange sites on the resin is reduced which results in a loss of exchange capacity and efficiency. An example of this problem is the poisoning of the anion resin by complex metal cyanides,⁶ especially the iron complex.

An ion exchange system of the types examined by this review would not be acceptable for use with the Thiokol cyanide waste treatment system. In addition to the problems of poisoning cited above, the low cyanide (< 2 mg/l) and high salt (10,000 to 20,000 mg/l) concentrations in the effluent of the Thiokol system would further complicate the situation since salt water is often used to regenerate the resins. Even though the resin may preferentially adsorb the cyanide and heavy metal ions, the high salt concentration provides a driving force sufficient to overcome the adsorptive power of the resin and the adsorbed species are discharged. No resin was found that was selective only to cyanide in a high salt environment.

Adsorption

Certain solids preferentially concentrate specific substances from solution to their interfaces. The intermolecular attractive forces between molecules of the substance adsorbed and the adsorbing solid are sufficiently great to "condense" the substance upon the surface of the solid and hold it there despite the efforts of the carrier medium to redissolve the material. Activated carbon was the only adsorptive material found in the literature search for the treatment of cyanide waste.

An adsorption method for the removal and destruction of cyanides using activated carbon has been reported.^{3, 4, 7} The reports indicate that the cyanide can be oxidized using activated carbon, oxygen, and the copper (cupric) ion. The copper ion forms a complex with the cyanide. The complex is then adsorbed on the activated carbon where it reacts with the oxygen to form CO_2 and NH_3 . The carbon can be regenerated as required.

Reverse Osmosis

Discovered in 1748, the osmotic phenomenon has been investigated by many people and the literature is replete with references regarding osmosis and reverse osmosis. The process of reverse osmosis (RO) is dependent on the availability of a semipermeable membrane which will reject the dissolved

materials of interest, which will pass sufficient quantities of liquid solvent, and which is compatible with the liquid solvent.

Reverse osmosis is used in plating operations to concentrate the diluted metal plating waste and to recover water and heavy metals for reuse. The concentrate is recycled back into the plating tank.^{2,6,8,9} Any waste concentrate from an RO unit on a plating line must be treated to remove substances such as cyanide prior to discharge to the environment.

One problem unique to the Thiokol system with regard to the use of an RO add-on unit is the relatively high residual chlorine concentration of the effluent from the basic cyanide destruct system. No RO membrane was found in the literature search which would adequately treat the effluent liquid and at the same time withstand the destructive attack of the residual chlorine.

Integrated System

Another method for the treatment of cyanide-containing wastewater is known as an integrated waste treatment process^{1,6}. The cyanide rinse water is treated with chlorine or sodium hypochlorite and returned for reuse to the rinse tanks. Settling tanks are used to precipitate the metal oxides, which can be recovered if desired. There is a salt buildup in conventional integrated systems and this can be removed periodically by dumping the liquid⁶ or by regularly discharging a small amount of the treated liquid. These systems have several advantages. The amount of discharged liquid is very small and a large quantity of rinse water is saved. The rinse tank has a high chlorine level and this destroys the cyanide immediately and eliminates many of the problems associated with cyanide dragout. The plated part can be washed with water after it emerges from the rinse tanks. The Thiokol system could be easily converted to an integrated system without many of the discharge problems of other chlorination methods.

Electrolytic Decomposition

Electrolytic decomposition is used in many applications to oxidize the cyanide^{1, 2, 6, 8, 9, 14}. It works very well in concentrated solutions but is very inefficient in dilute solution and the effluent generally must be treated by conventional methods for final cyanide removal¹. The Thiokol system could be operated as an electrolytic system for the direct decomposition of cyanide but because of the low cyanide level, this is not the preferred approach.

ANALYTICAL TECHNIQUES

A second literature review was made of analytical procedures which could be used for measuring cyanide in the prototype tests. Several of these methods can be used on a routine analysis with a high degree of accuracy.

Distillation

Distillation is an important part of the analytical procedure because it not only isolates cyanide from most interferences (such as the chloride ion which is present in the Thiokol system), but converts most cyanide complexes into the simple cyanide that is measured by titration or color test. The standard distillation method used is the Serfass¹⁶ procedure. A modification was made by Elly¹⁷ to the standard method which gave a higher cyanide yield at levels below 0.1 mg/l for complex cyanides. Another method¹⁸ was developed which will break down the complex cyanides of cobalt and iron. This method can detect down to the parts-per-billion levels of simple and complex cyanides. Ultraviolet light is used to irradiate the sample to break down the complex cyanides during this distillation.

The literature review did not reveal any discovery by others of any errors in the Serfass distillation method due to the generation of chlorine when the sulfuric acid is added. Such errors were reported¹¹ in Thiokol's previous work. It has been found that the errors in the Serfass

distillation appear only when chlorate is present. It was found that the electrolytic cell generates small amounts of chlorate during the generation of hypochlorite, and chlorine is released from the chlorate during the Serfass distillation because of the very low pH used in that process. Tartaric and phosphoric acids have been used for distillation. Tartaric acid was evaluated in this study as a method of measuring cyanides in the Thiokol system effluent.

Analysis

There are a number of methods for measuring the cyanide in a sample after it has been distilled. A review of the different titration and colorimetric methods was made by Bark and Higson.¹⁵ The application of a selective ion electrode is discussed in several reports.^{19, 20, 21, 22} This method is rapid and can measure very low levels of free cyanide. A spectrophotometric method²³ was found using a linear starch iodine system.

Serfass and colleagues¹⁶ recommend that the modified Liebig titration method using the paradimethylaminobenzalrhodanine indicator be used for samples with a cyanide concentration greater than 1 mg/l CN and that the colorimetric method using pyridine-pyrazolone be used below this level.

LABORATORY TESTS

In the course of the development of the prototype cyanide waste treatment system, it was necessary to evaluate the effects of certain interfering materials and of various treatment processes. The details of these tests are presented in Appendix A. A brief summary of the results is outlined below.

Carbonate and Bicarbonate

It was discovered in earlier Thiokol investigations that carbonate and bicarbonate ions in the electrolyte reduce the chlorine generating efficiency, and hence the cyanide destruct capacity, of an electrolytic cell.

Thus, if an electrolytic system were on-line at a cyanide waste treatment facility operating at design capacity, any significant increase in the bicarbonate concentration of the electrolyte could cause the system to discharge wastes that were only partially treated. A preliminary study was made to determine the magnitude of the carbonate-bicarbonate interference in cell operation. Minimal effects were observed at low concentrations of bicarbonate (1,500 mg/l) where the system would normally operate. However, at higher concentrations (6% bicarbonate) the Engelhard cell that was tested showed a 60% drop in chlorine generation rate. With the PEPCON cell, the reduction was approximately 10 to 1 under the same test conditions.

Activated Carbon, UV, Temperature, and pH

A study was made to determine the effects of activated carbon, UV light, temperature, and pH on the treated effluent from the prototype system. The uncertainty found in the colorimetric analysis had not been completely understood nor eliminated at this time in the program. Therefore, only the following general observations can be supported by the data of this study (see Appendix A).

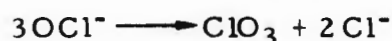
1. Improved treatment can be achieved at a pH of 7.3 and a temperature of 120°F.
2. There is an increase of measurable cyanide from the UV exposure and a reduction from carbon treatment.
3. A pH of about 7 is the best of the levels tested^{3, 7, 11} for cyanate removal.

ANALYTICAL METHODS STUDIES

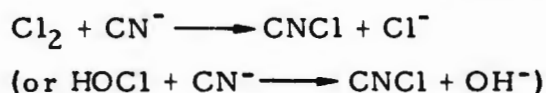
Samples of cyanide plating waste were obtained from Hill AFB. These samples were analyzed for the purpose of comparing the tartaric acid method with the sulfuric acid method of analysis on cyanide wastes that were previously treated for cyanide removal by alkaline chlorination.

The main reason for analyzing these types of waste materials was to determine the effect of conventional alkaline chlorination on the level of chlorates in the liquid, hence the analytical precision that could be assured by the standard sulfuric acid method.

No chlorates were found in the treated liquid. This fact provides some evidence that the sulfuric acid method may be satisfactory for evaluating the effectiveness of alkaline chlorination. However, the data are not conclusive for at least two reasons. First, one method for the production of chlorate involves the self-oxidation of hypochlorite:²⁵



Thiokol laboratory tests have shown that chlorates can be produced during alkaline chlorination. Second, the above reaction, which occurs very slowly at low temperatures and at a pH greater than 7, must compete for the hypochlorite reactant with the main cyanide destruct reaction:



The rate of this reaction is essentially independent of the pH of the solution and it occurs practically instantaneously. Perhaps as the cyanide concentration approaches discharge levels, more hypochlorite would be available for the chlorate reaction, and the analytical problems caused by the chlorates would increase.

The results of the analyses of the above samples are shown in Table 1. Where no alkaline chlorination was used, HAF-2, and for HAF-1 with very high dilution, the analytical results show remarkable agreement between the two test methods. After the designated treatment time (using a simple chlorine injector to feed the chlorine into the cyanide tank), the data show the tartaric acid method to be inadequate for this material if it has first been chlorinated. A residue which had a pH buffering effect remained in the sample after the addition of the tartaric acid. The amount of tartaric acid called for in the analysis was insufficient to overcome this

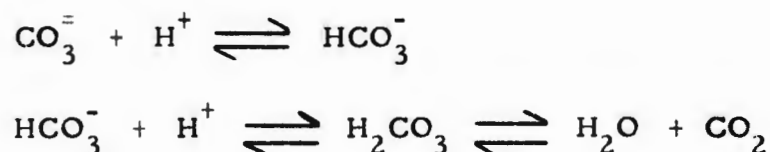
TABLE 1
ANALYSIS OF CADMIUM PLATING WASTE

Sample Identification	Dilution	Cyanide Concentration (mg/l)		
		Tartaric Acid Distillation		Sulfuric Acid Distillation
		Standard Method	With Scrubber	
HAF-1	1:4	515	-	1,678
HAF-1	1:100	1,480	1,460	1,340
HAF-2	1:1000	39,600	39,800	39,800
HAF-3	1:4	51	47	1,340
HAF-3	1:100	860	840	1,360
HAF-3 Residue	1:100	-	-	880

HAF-1: Alkaline Chlorination for Approximately 20 Days.
HAF-2: No Alkaline Chlorination.
HAF-3: Alkaline Chlorination for 22 Days.
HAF-3 Undissolved Solids from Tartaric Analyses of
Residue: HAF-3.

buffer and reduce the pH to an adequate level for the analysis. Perhaps additional tartaric acid could be added to eliminate the residue and thereby render the solution amenable to the tartaric acid method but this would constitute a significant departure from the standard method, and further research would be required to restandardize the method under these conditions.

During the addition of the tartaric acid to HAF-1 and HAF-3 a very strong effervescence was observed along with the formation of a very heavy, slightly yellowish precipitate. The raw sample had a yellow cast to begin with. The effervescence was characteristic of the familiar carbonate decomposition process:



To insure that some of the effervescence was not caused by the evolution of HCN, all of the gases from the test flask were forced to pass into the caustic solution in the distillate flask wherein the gases could be scrubbed and the cyanide removed. Table 1 shows the comparison test results as "Standard Method" and "With Scrubber." The data show the effervescence to be caused by something other than HCN since the cyanide analyzed by both approaches is essentially the same.

If the effervescence is caused by carbonate decomposition, the carbonate would act as a buffer and would overpower any acidification attempts until the carbonate was exhausted. The effects of this buffering action were not observed in the sulfuric test because of the large excess of acid added. However, pH control is important in the tartaric method. With the tartaric acid method pH is reduced to about 5 and then a small excess of tartaric acid is added to reduce the pH to approximately 2.5. The carbonate buffer could easily overpower the acid, and the result would be a solution pH not low enough to free some of the complexed cyanide.

This reasoning is further confirmed by the agreement in the results of the analyses of highly diluted samples and for samples which had not been chlorinated and, therefore, contained little carbonate.

For HAF-1, the numbers reported under sulfuric acid distillation vary from 1,340 for 1:100 dilution to 1,678 for 1:4 dilution. The 1:100 sample was analyzed one weekend later than the 1:4 sample and most probably the residual chlorine in the sample (from the alkaline chlorination) destroyed some additional cyanide.

During the tartaric analyses of HAF-3 the solids formed did not totally redissolve as they did in the sulfuric test undoubtedly because of the high pH discussed above. This residue was redistilled by the sulfuric acid method to determine if unreacted cyanide complexes were present. The analysis revealed that a significant amount of cyanide had not reacted during the tartaric distillation (see Table 1). For this test, the residue from both the "standard method" sample and the "with scrubber" test were combined. Assuming each sample contributed half of the cyanide determined by the sulfuric method, the sum of the tartaric cyanide and one-half the sulfuric cyanide is a number which agrees very closely with the total cyanide determined by the sulfuric acid method initially, i. e.,

$$(840 \text{ to } 860) + 1/2 (880) = 1,280 \text{ to } 1,300 \text{ (vs } 1,360 \text{ for sulfuric)}$$

The sulfuric acid distillation method has given very erratic data in this program as well as in prior Thiokol work. At times, no data were obtainable because the titration end-point was obscured by two interfering reactions. The first one observed during the analysis is the bleaching effect of any residual chlorine on the chemical color indicator, which required the addition of more indicator. The second interference was a "clouding" effect on the sample caused by the precipitation of AgCl . AgNO_3 is the titrant in the analysis. Any chloride in the sample, e. g., the reaction product of chlorine and indicator, would cause solid AgCl to form and precipitate.

The presence of chlorate produced by the treatment process is most probably the cause of this problem. When the sample is acidified in this procedure, the chlorate is decomposed into chlorine or some other species of similar oxidizing power. The cyanide in the sample is then oxidized. The subsequent analysis would then indicate that there is less cyanide than was actually present in the initial sample. In cases of very high chlorate levels (above 200 mg/l) chlorine is released in such quantities that some is boiled over into the distillate. During the AgNO_3 titration, AgCl is formed, which obscures and distorts the end-point. Erratic color development in the colorimetric analysis caused by this phenomenon significantly reduces the accuracy of the analysis.

To verify that the chlorate ions were the cause of these analytical problems, sodium chlorate was added in increasing quantities to copper plating waste containing approximately 5 mg/l cyanide. The samples were then distilled by both the tartaric acid distillation method and the sulfuric acid distillation method. Data are shown in Figure 2.

These data show that, as the NaClO_3 concentration increases, the cyanide level decreases at an almost linear rate in the sulfuric acid distillation but remains constant in the tartaric acid distillation. Chlorate decomposition occurs most rapidly in the highly acidic condition below pH of 2. In the tartaric acid distillation the pH does not reach 2 while in the sulfuric acid method it is considerably below 2.

Goulden, Afghan and Brooksbank¹⁸ describe a method of using ultraviolet light to help break down the complex cyanides in the distillation step for cyanide analysis. In an attempt to adapt this modification to the methods being used in this study, a UV irradiation cell was incorporated in the H_2SO_4 distillation apparatus and also in the tartaric acid distillation apparatus. Samples of nickel plating waste and copper plating waste were distilled by both methods. This was done with and without UV irradiation and with and without chlorate. Data are presented in Table 2.

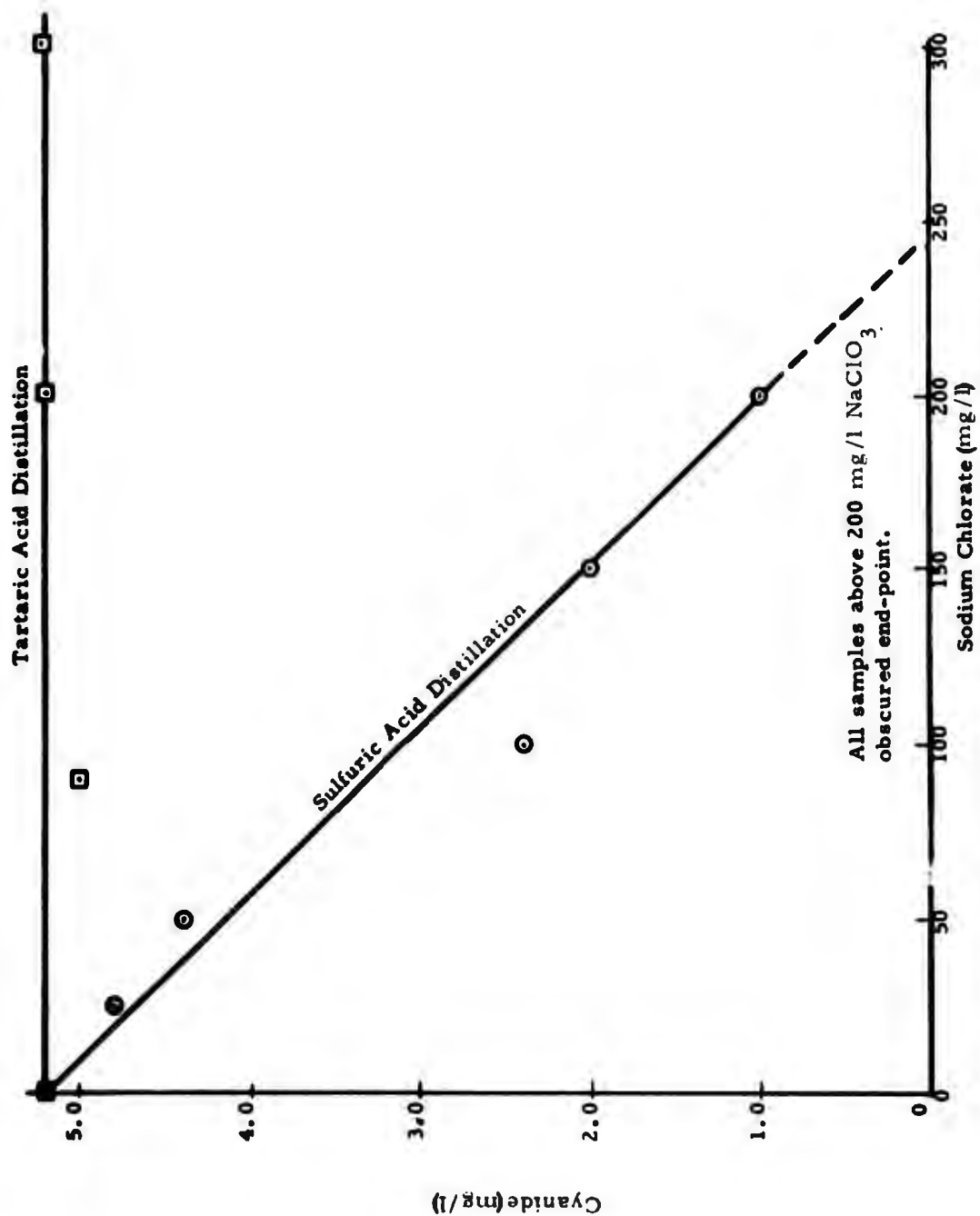


Figure 2. Effect of NaClO_3 in Distillation of Copper Plating Waste

TABLE 2
EFFECT OF UV IRRADIATION
ON CYANIDE DISTILLATION

<u>Sample Treatment Description</u>	<u>CN⁻ Concentration (mg/l)</u>	
	<u>Sulfuric</u>	<u>Tartaric</u>
Ni waste approx 1.50mg/l CN ⁻ - No ClO ₃ - No UV	1.30	1.25
Ni waste approx 1.50 mg/l CN ⁻ - 100 mg/l ClO ₃ - No UV	0.97	1.25
Ni waste approx 1.50 mg/l CN ⁻ - 100 mg/l ClO ₃ - With UV	0.27	-
Cu waste approx 5 mg/l CN ⁻ - 100 mg/l ClO ₃ - No UV	2.00	5.20
Cu waste approx 5 mg/l CN ⁻ - No ClO ₃ - With UV	5.50	-
Cu waste approx 5 mg/l CN ⁻ - 100 mg/l ClO ₃ - With UV	1.60	-
Ni waste approx 6.5 mg/l CN ⁻ - No ClO ₃ - With UV	-	3.50
Ni waste approx 6.5 mg/l CN ⁻ - 100 mg/l ClO ₃ - No UV	2.25	6.60

These data indicate that UV irradiation does improve the conversion of complex cyanide compounds to simple cyanides in the sulfuric acid distillation when chlorate is not present. Where chlorate is present, the UV apparently accelerates the decomposition of chlorate and increases the destruction of cyanide. UV irradiation does not work with the tartaric acid distillation, as the tartaric acid is decomposed by UV irradiation. Because of the high chlorate level, the UV method is not acceptable for cyanide analysis on effluent treated with a chlorine-generating electrolytic cell.

The data obtained in measuring cyanide by the colorimetric method at first showed considerable inconsistency. To determine the cause of variations between similarly treated samples, five aliquots of a single distilled sample were analyzed by the colorimetric method. The data obtained (Table 3) showed a great deal of disagreement. This test was repeated by a second analyst to determine whether technique had a significant effect on the results. The data here were similarly erratic.

The standard colorimetric method calls for a pH adjustment of the sample after distillation to somewhere within the range of 6 to 7. An investigation was made to determine what, if any, effects the pH had on the colorimetric analysis results. As one can see from the data in Figure 3, a significant difference in measured cyanide concentrations was observed as the pH was varied. When the same series of tests was performed on a standard solution of KCN, a much smaller variation was observed (Figure 3). A comparison of these results with the results shown in Appendix A, Table A-10, indicates that the variations shown as resulting from a given treatment method could have been caused by the analytical method instead.

In determining the cyanide concentration of a given material by the colorimetric method, a standard calibration curve is prepared by plotting the absorbance values of five standard KCN solutions ranging from $0.2 \mu\text{g CN}^-$ to $1.0 \mu\text{g CN}^-$ and comparing the absorbance of the sample to the

TABLE 3
Variation of CN^- Measured by Colorimetric
Method on Duplicated Samples

<u>Sample Description</u>				<u>CN^- Measured (mg/l)</u>
M85 - 5/29/74 - 1000			#1	0.108
"	"	"	#2	0.258
"	"	"	#3	0.048
"	"	"	#4	0.080
"	"	"	#5	0.168

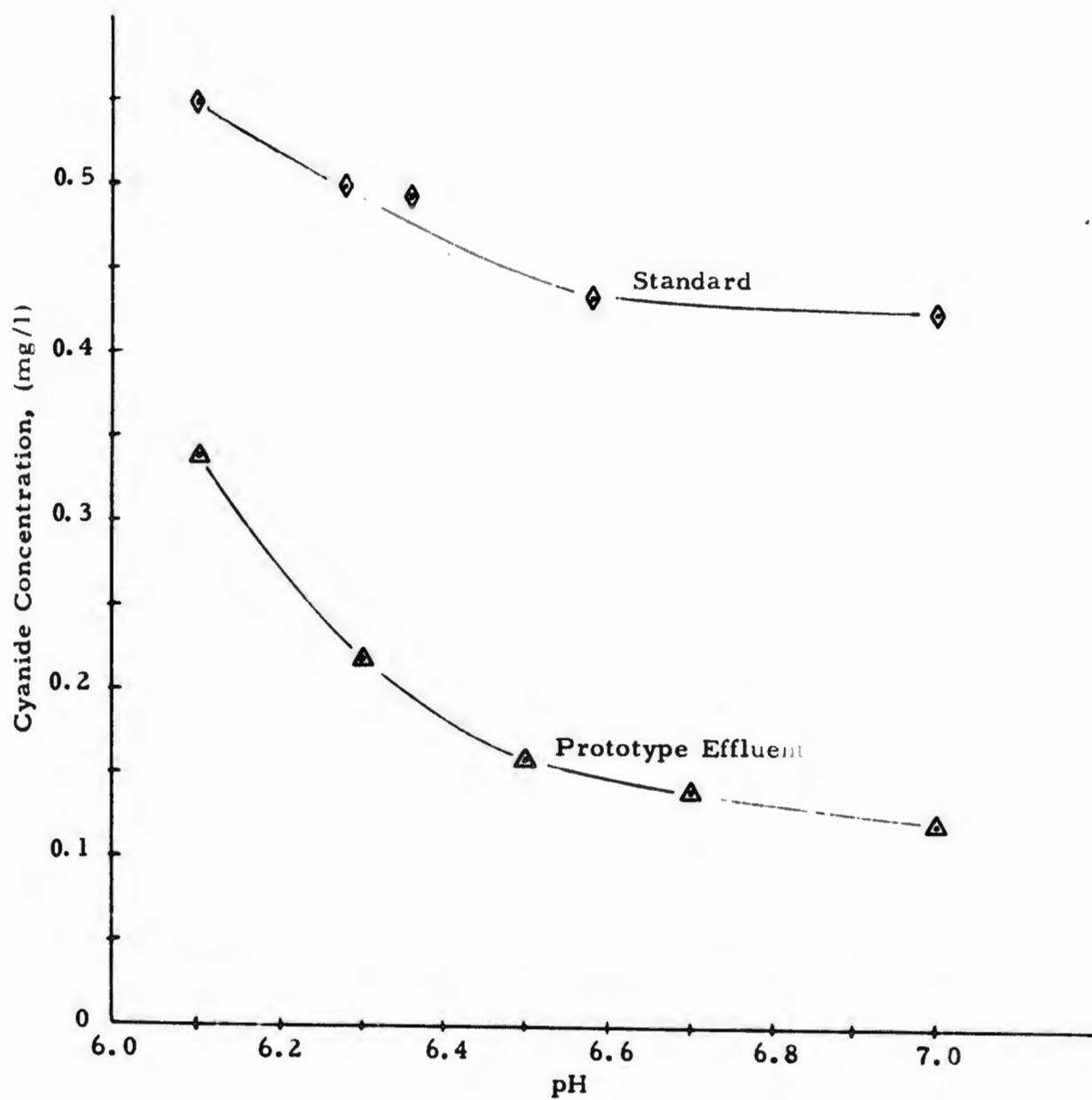


Figure 3. Effect of pH on Colorimetric Cyanide Analysis

calibration curve. Curves were prepared at pH 6.10 and 6.85. Data are shown in Figure 4. The data show no significant effect of pH on the calibration curve.

A precision study was made to determine the variation in the colorimetric method. Five tests were made using aliquots from the same sample and at the same conditions. The data are shown in Table 4. The repeatability was observed to be within 0.020 mg/l cyanide.

The colorimetric analysis procedure also calls for a period of approximately 20 minutes to allow color development after the addition of reagents. A test series was set up where color development was monitored at five minute intervals over a period of 40 minutes to determine the effect of time on color development. Data are presented in Figure 5 which indicate that time control is not a critical factor and reaction time can be allowed to vary between lower and upper limits of 20 and 35 minutes, respectively.

The next question considered was whether the low cyanide level measurement was at all accurate. In order to answer this question, a sample of treated product was prepared and distilled. Measurement by titration with standardized 0.02N AgNO_3 in triplicate samples confirmed a concentration of 20.0 mg/l cyanide. A 2 ml sample of this material was diluted to 100 ml to produce a concentration of approximately 0.4 mg/l CN^- . This diluted sample was then measured colorimetrically at pH's varying from 5.5 to 6.50. The data shown in Figure 6 represent an average of three determinations and establish the accuracy of the colorimetric method when the pH of the color reaction is controlled between pH's of 5.75 and 6.25.

Preliminary results from a closer examination of just the distillation portion of the analysis procedure have identified a further cause of error, namely, an effect of the sulfite used to neutralize the chlorine in the sample. The sulfite apparently distills over into the collection flask and inhibits the color forming reactions used to measure the cyanide.

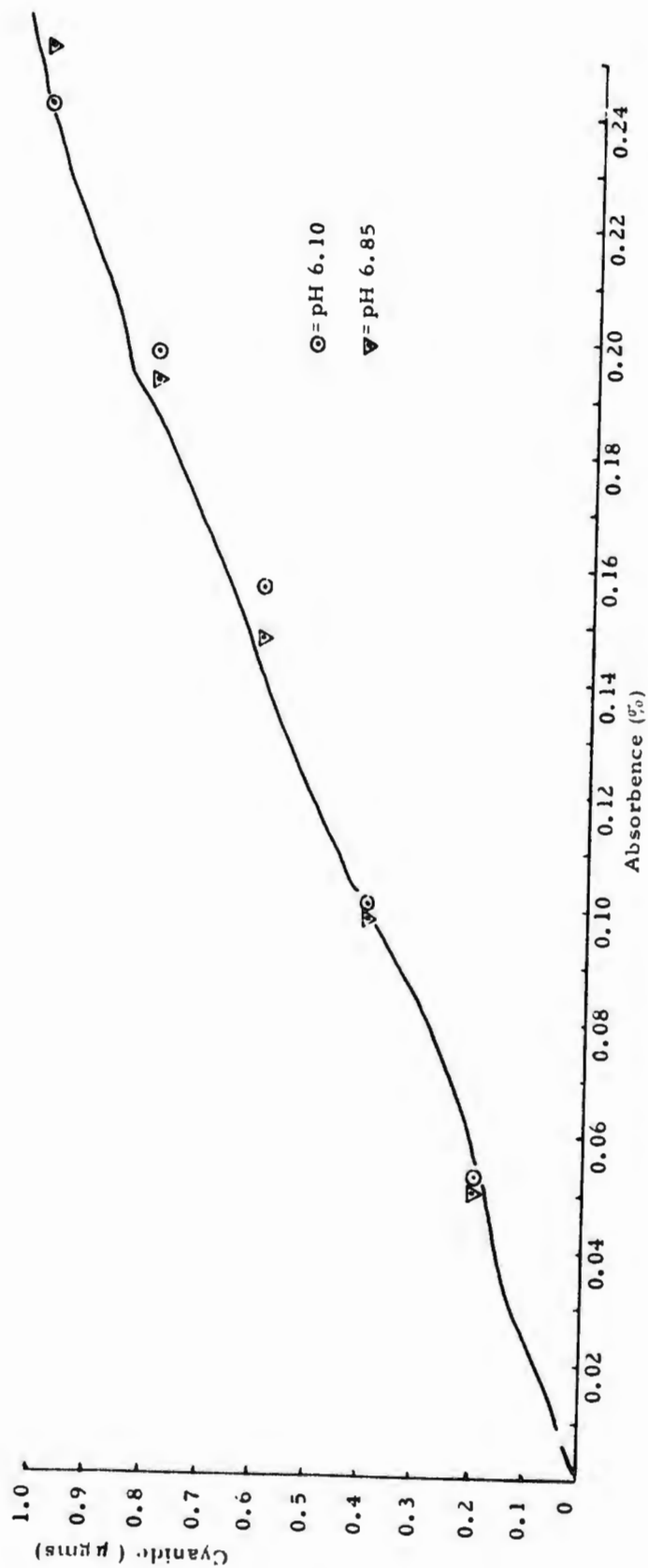


Figure 4. Effect of pH on Calibration Curve

TABLE 4
Colorimetric Method Precision Study

<u>Sample No.</u>	<u>Cyanide (n.g/l)</u>
1	0.440
2	0.425
3	0.425
4	0.425
5	0.420

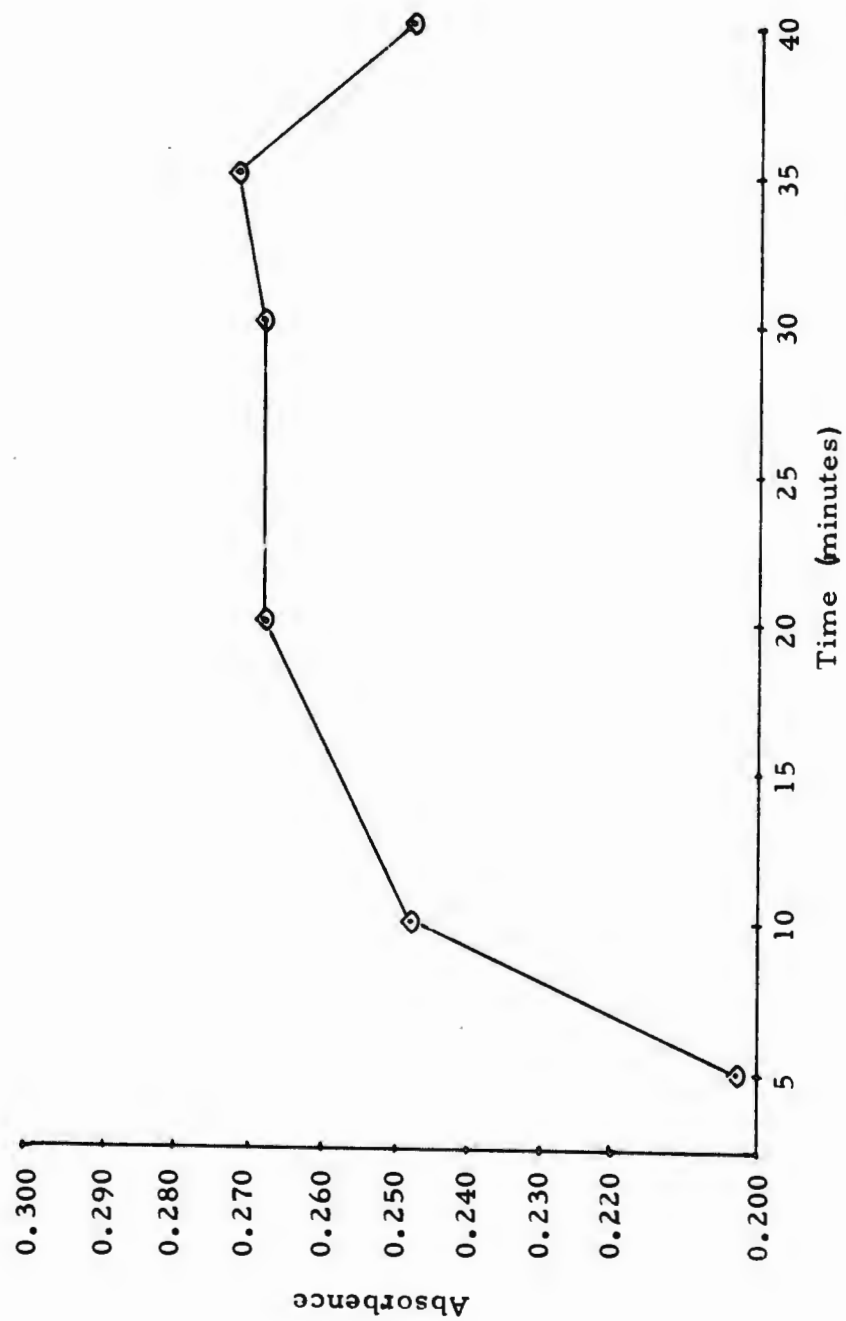


Figure 5. Effect of Time on Color Development in Colorimetric Cyanide Analysis

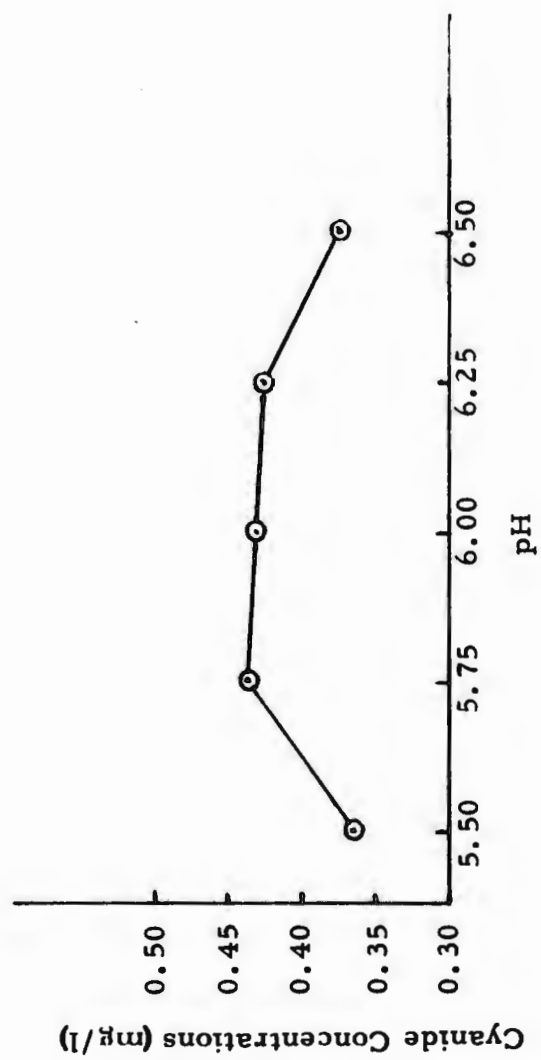


Figure 6. Accuracy of Colorimetric Analyses

When a sample is withdrawn from a destruct system for subsequent cyanide analysis, it is important to immediately stop the activity of the oxidizing agent used to destroy the cyanide. The oxidizing agent is, of course, chlorine (hypochlorite) in the Thiokol system. Also, it is necessary to destroy any residual chlorine in a sample before distillation since chlorine boils over in the distillation and interferes with the analysis. The procedure normally used is to add a small quantity of sodium sulfite powder and then check the sample for chlorine by adding orthotolidine. If chlorine is still present, the procedure is repeated until no more chlorine is indicated. This technique is not precise and may allow the addition of an excess of the sodium sulfite. In order to determine if the Na_2SO_3 interfered in the analysis, a sample of liquid effluent from the prototype was passed through an activated carbon column which removed all residual chlorine. This step probably destroyed some cyanide but was necessary to provide a consistent, chlorine-free sample. A portion of this product was then distilled without Na_2SO_3 and an equal portion was distilled after the addition of a small quantity of Na_2SO_3 . This would constitute an excess of sulfite since there was no chlorine with which to react. The samples were distilled and analyzed colorimetrically and as the data in Table 5 show, the sample with sodium sulfite yielded no color development while the sample with no sulfite contained more than 0.5 mg/l cyanide. This indicates that excess sulfite exerts a definite effect on the analysis.

Since the Na_2SO_3 added to the above sample constituted an excess because no chlorine was present, samples were then tested to determine if precise chlorine destruction by Na_2SO_3 would allow accurate determination of cyanide.

Chlorine was destroyed in duplicate samples. The first sample was passed through activated carbon to effect the chlorine destruction. The second sample was divided into triplicate aliquots. The Na_2SO_3 that was required to neutralize the chlorine was precisely measured by titrating one of the aliquots to the end-point using the potassium iodide method.

TABLE 5
Effects of Excess Na_2SO_3 on Colorimetric
Cyanide Analysis

Without Na_2SO_3		With Na_2SO_3	
Aliquot	CN^- Concentration (mg/l)	Aliquot	CN^- Concentration (mg/l)
#1	0.600	#1	Nil
#2	0.575	#2	Nil
#3	0.545	#3	Nil

TABLE 6
Comparison of Precise Neutralization of Chlorine
by $\text{Na}_2\text{SO}_3/\text{KI}$ Titration vs Activated Charcoal

$\text{Na}_2\text{SO}_3/\text{KI}$ Titration		Activated Charcoal	
Aliquot	CN^- Concentration (mg/l)	Aliquot	CN^- Concentration (mg/l)
#1	0.992	#1	0.185
#2	0.982	#2	0.180
#3	0.992	#3	0.175

The same amount of sulfite was added to the other aliquots. These three aliquots and three aliquots from the carbon treated sample were then distilled and analyzed for cyanide.

Previous data would predict that some of the cyanide would be removed by the carbon. If, therefore, a higher level of cyanide were measured in the carbon treated samples than in the sulfite treated samples, it would indicate that the sulfite method would not be acceptable. A higher cyanide level in the three sulfite treated aliquots would support the conclusion that the sulfite method is adequate so long as the sulfite is not added in excess.

The data as shown in Table 6 verify that this is the case as the Na_2SO_3 treated samples yielded an average of 0.989 mg/l CN^- with 0.010 deviation while the carbon treated samples yielded 0.180 mg/l CN^- with 0.010 deviation. The conclusion from this experiment is that precise neutralization of chlorine by Na_2SO_3 is probably essential for reliable determination of cyanide by the colorimetric method.

In order to further verify these conclusions, a 100 ml sample of material determined by the colorimetric method to contain 2.5 mg/l CN^- was added to 100 ml of 20.0 mg/l material. One hundred milliliters of this solution were distilled and analyzed by titration. The sample was measured by titration with 0.2N AgNO_3 . Two determinations yielded 22.52 and 22.54 mg/l CN^- . The theoretical yield is 22.50 mg/l CN^- .

The experimentation with the various methods of cyanide analysis led to the conclusion that the greatest accuracy and precision could be attained by using the tartaric acid method for distillation, the silver nitrate method for titration, and the colorimetric method for analysis of cyanide at high dilution. To attain this accuracy and precision, the chlorine (hypochlorite) in the sample must be neutralized precisely. The potassium iodide-sodium sulfite titration method is recommended. Because the colorimetric analysis is sensitive to changes in pH, the pH must be precisely controlled to achieve accuracy with

this method of analysis. Experimentation shows that the pH should be maintained at a constant value from sample to sample. A pH of 6.1 was found to give the best results. These analytical procedures were used during the Field Test program of the destruct system at Hill AFB.

It should be noted that the studies involving activated charcoal, ultra-violet irradiation, temperature, and pH variation which were conducted before the problems involving sodium sulfite and pH in the analysis procedures were isolated may be of limited value. The data on these studies are questionable since one cannot be sure the effects indicated by the data are actual effects of the treatment or are a result of a composite of errors induced by the interferences in the analyses. However, the data generated by titration with AgNO_3 are reliable.

All data accumulated in the field tests of the prototype system are accurate since the modifications to analytical techniques developed by studies of interference effects of pH and Na_2SO_3 were incorporated in the analysis procedures.

PROTOTYPE SYSTEM STUDY

DESIGN OBJECTIVES

The cyanide destruct system is intended to treat cyanide contaminated rinse water associated with Air Force electroplating wastes. The rinse water is assumed to contain a variety of metal cyanides, cyanates, and organic stripping compounds. System requirements are tabulated below.

Influent

CN ⁻ Conc	<500 mg/l
Process Rate	0.5 gpm

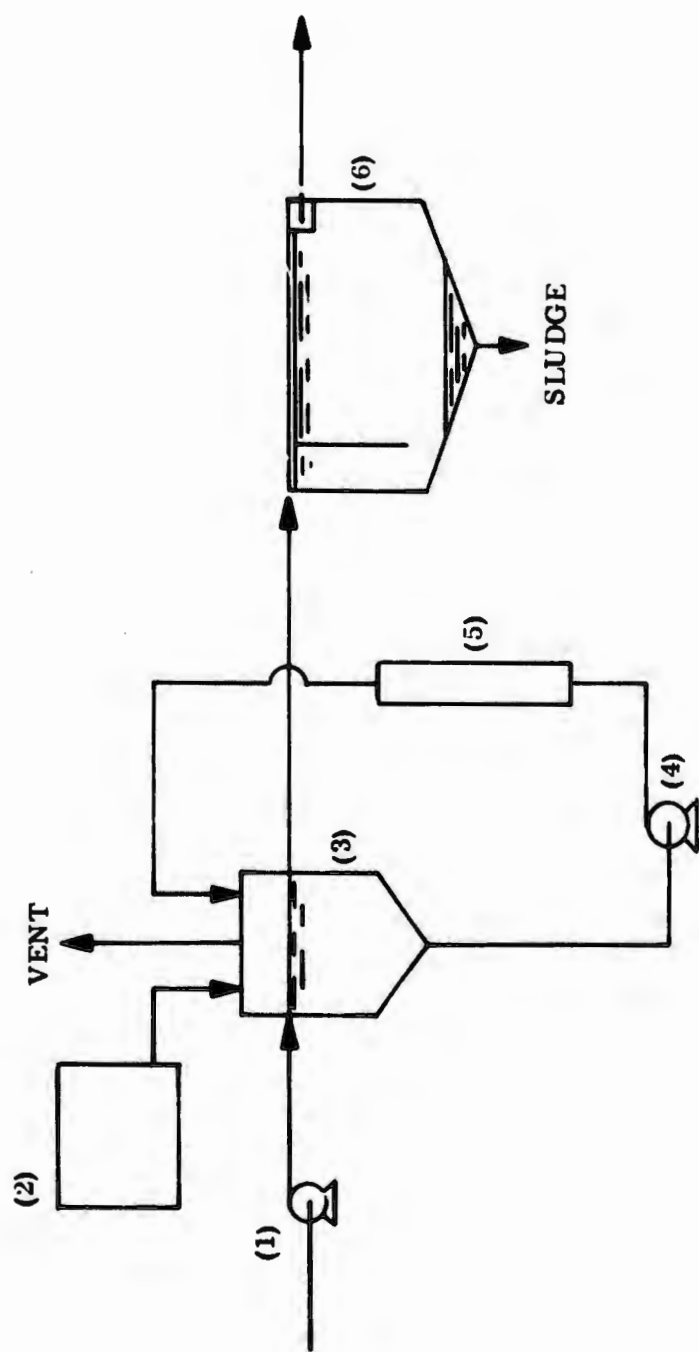
Effluent

CN ⁻ Conc	<1 mg/l
CNO ⁻ Conc	<20 mg/l
Residual Chlorine	≈100 mg/l
Suspended Solids	<50 mg/l
Temperature	<100°F
Salt Concentration	2%

DESIGN CONCEPT

A process schematic of the cyanide destruct system is presented in Figure 7. The cyanide waste is metered to the chlorination tank by means of a positive displacement pump. Salt is added to the tank by a volumetric dry chemical feeder to maintain a salt concentration of two percent. Chlorine and caustic are generated electrolytically from the salt water solution and are reacted under slightly alkaline conditions to oxidize the cyanide contaminants. Hydrogen gas, also generated from the electrolytic cells, is vented from the chlorination tank by forced air convection. Solids formed during the treatment process; e. g., metal hydroxides, are removed from the effluent by gravity sedimentation.

The system is operated manually. The electrolytic cells are protected by low flow and overvoltage indicator/controllers which will shut down the



- | | |
|-----------------------|-----------------------|
| (1) PROCESS PUMP | (5) ELECTROLYTIC CELL |
| (2) SALT FEEDER | (6) SETTLING TANK |
| (3) CHLORINATION TANK | |
| (4) RECYCLE PUMP | |

Figure 7. Process Flow Schematic

entire system if insufficient flow or high voltage (low salinity) is detected. A temperature indicator, cumulative process timer, dc-volt meter and dc-ammeter are provided.

SELECTION AND SIZING OF COMPONENTS

A description of the major items of process equipment and the selection criteria are presented below:

Process Pump

The process pump is a progressive cavity, positive displacement pump, Model BA-100, manufactured by the Moyno Pump Division of Robbins & Myers, Inc. It is driven by an SCR controlled, variable speed dc-motor. The displacement of the pump is 0.072 gal/100 revolutions at a discharge pressure of 10 psig. A rotational speed of approximately 685 rpm is required to deliver the required process rate of 0.5 gpm.

Salt Feeder

The salt feeder is a volumetric dry chemical feeder, Model 25-04, manufactured by BIF Products. Material is fed from an agitated storage hopper by a rotating horizontal feed helix. The unit is equipped with a variable rate setter which starts and stops the feeder motor in a repeating cycle for feed rate control. A salt delivery rate of 5 lb/hr or $0.10 \text{ ft}^3/\text{hr}$ is required to maintain a salt concentration of two percent. A helix diameter of 0.75 inches and a rotational speed of 10.5 rpm was selected for this application. This configuration will deliver $0.10 \text{ ft}^3/\text{hr}$ at a rate setting of 90 percent.

Chlorination Tank

The chlorination tank is a 50 gallon, bottom discharge, polyethylene vessel with gravity overflow at the 40-gallon level. The tank cover contains a salt addition spout and an air vent duct.

Recycle Pump

The recycle pump is a stainless steel, frame-mounted centrifugal, Model D-511, size 1-1/4 x 1 x 5, manufactured by Worthington Pump International. The pump capacity is 20 gpm at a discharge pressure of 26 psig which is compatible with either electrolytic cell option discussed in the following paragraph.

Electrolytic Cells

Two sources of electrolytic cells were considered for the system: Pacific Engineering and Production Company of Nevada (PEPCON) and Engelhard Industries (Chloropac). A summary of the two cell's characteristics is given below:

	<u>PEPCON</u>	<u>Chloropac</u>
. Cathode Material	Copper	Titanium
. Anode Material	Lead Oxide	Platinum
. Power Required	500 amp x 6 volt	200 amp x 12 volt
. Capacity, 90% Efficiency	31 lb Cl ₂ /day	25 lb Cl ₂ /day
. Capacity, 50% Efficiency	17 lb Cl ₂ /day	14 lb Cl ₂ /day
. Life	2 years	5 years

Illustrations of the two cells are given in Figures 8 and 9. The Chloropac cell was selected for use in the cyanide destruct system because of the longer effective life and the improved durability of the components.

The maximum cyanide mass flow to the destruct system, based upon a process rate of 0.5 gpm and a maximum cyanide concentration of 500 mg/l, is 3 lb CN/day. Assuming a cumulative (CN⁻, CNO⁻, metal ion, and organic) chlorine demand of 10 parts chlorine per 1 part cyanide, the prototype system must be capable of generating approximately 30 lb chlorine/day. Based upon a cell efficiency of 50 percent, 1.8 PEPCON cells or 2.1 Chloropac cells would be required. Two Chloropac cells were selected. These cells are

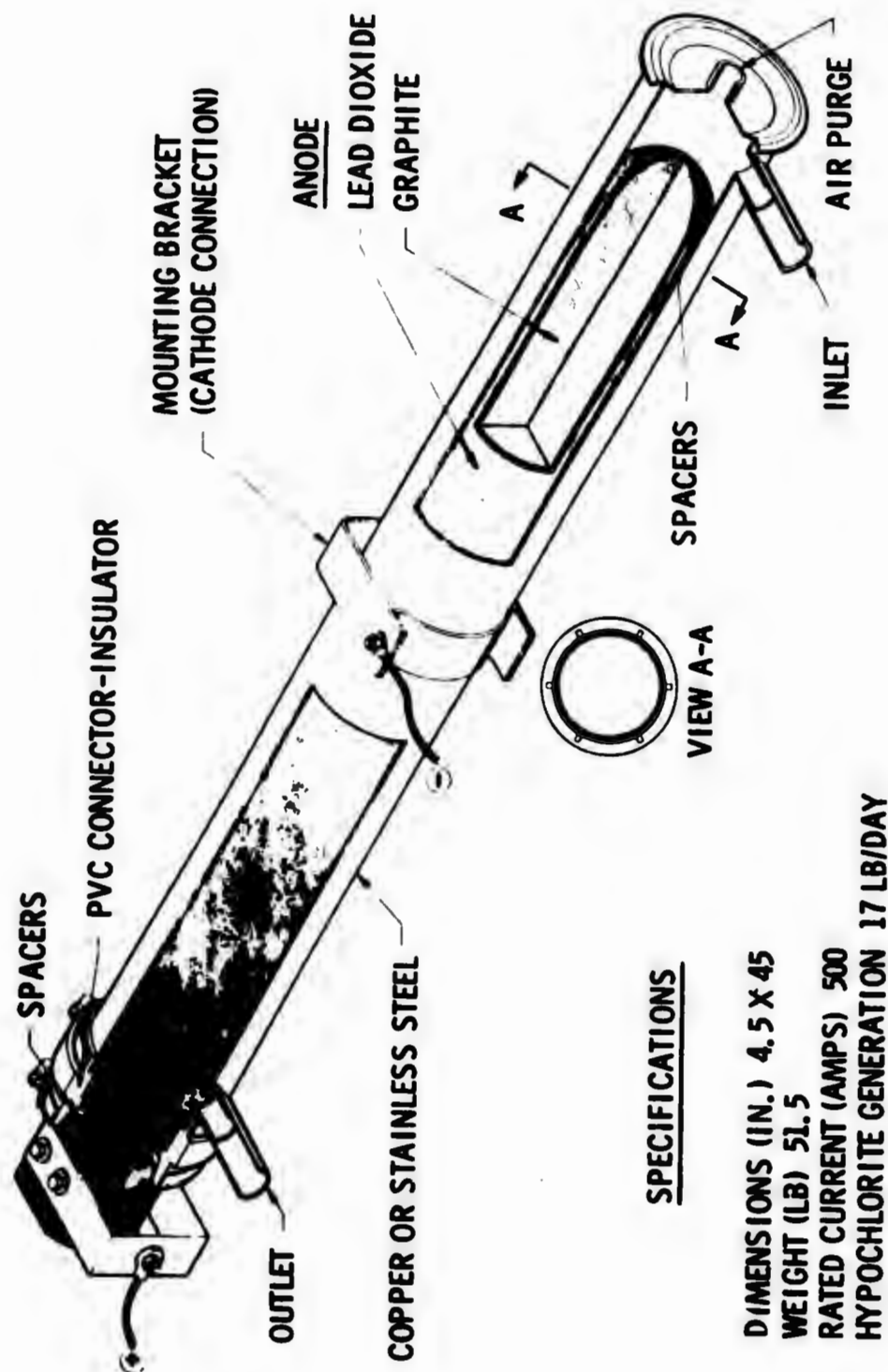


Figure 8. Standard PEPCON Cell

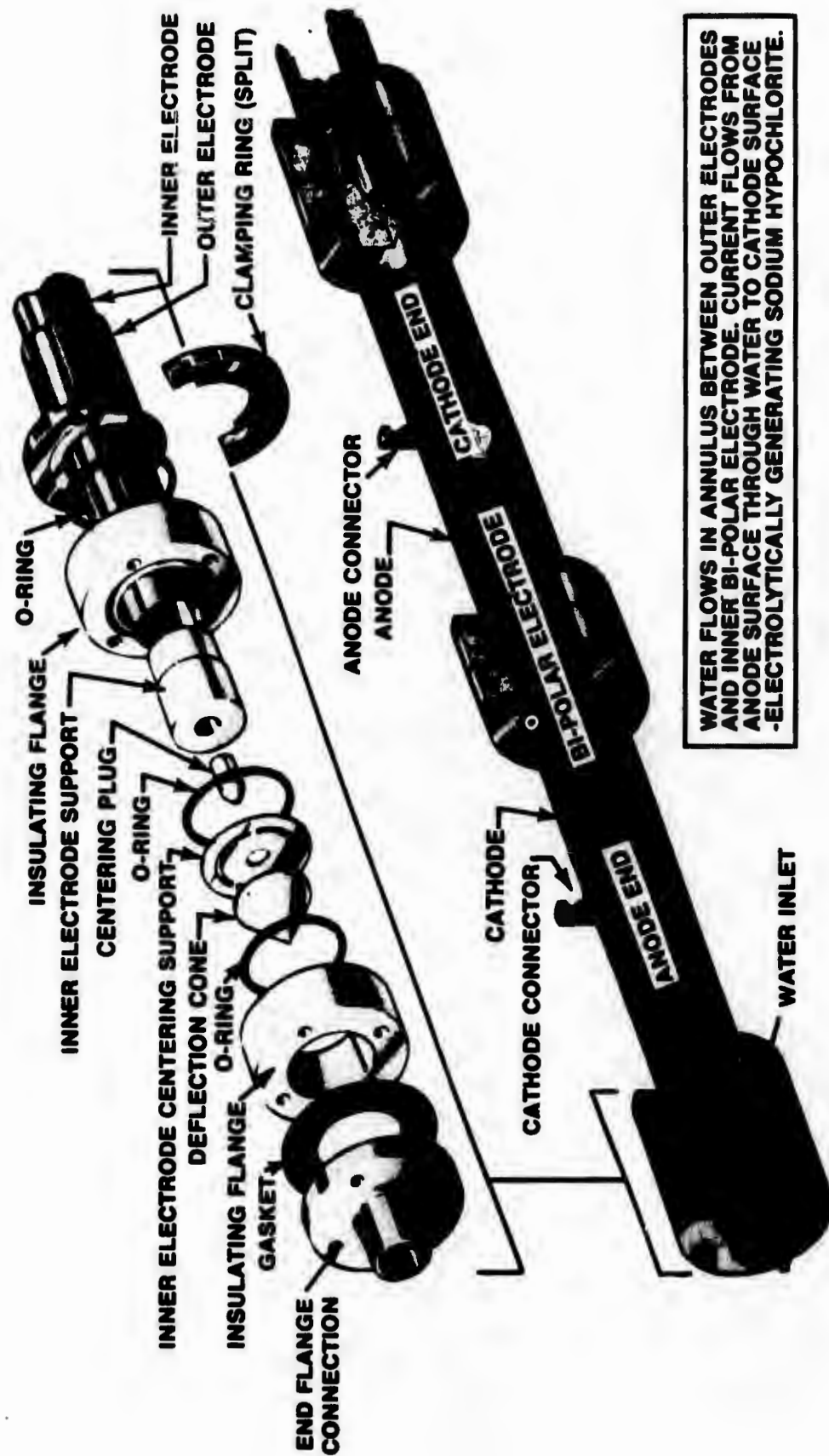


Figure 9. Standard Engelhard Cell

powered by a Model 50682-2 dc-power supply manufactured by Engelhard Industries.

Control System

The control system consists of the following three major components:

- 1) Control cabinet
- 2) Engelhard power supply and cells
- 3) Stepdown transformer with circuit breakers

Additional components not specifically classed as control units are the BIF salt feeder, the recycle pump motor, the feed pump motor, and the sludge pump motor.

Primary power required for the system is 440 volt, 3 phase, supplied from a 20 amp disconnect breaker. The installation at Hill AFB drew power from a General Electric Armor-Clad Plug-In busway that was a permanently installed power distribution network.

The system can best be described in outline form as follows:

Control Cabinet (Photo No. 1)

- . Houses all the motor starters, relays, temperature controllers, switches, indicator lamps that are used in operating the system.
- . Provides the central enclosure for terminating power and distributing control power to the operation portions of the system.

Engelhard Power Supply (Photo No. 2)

- . Generates the low voltage, high current required by the electrolytic cells.
- . Houses the cell overvoltage and flow protection circuits that are part of the control system.

The power supply incorporates safety input power and cell power breakers as part of this subsystem. The

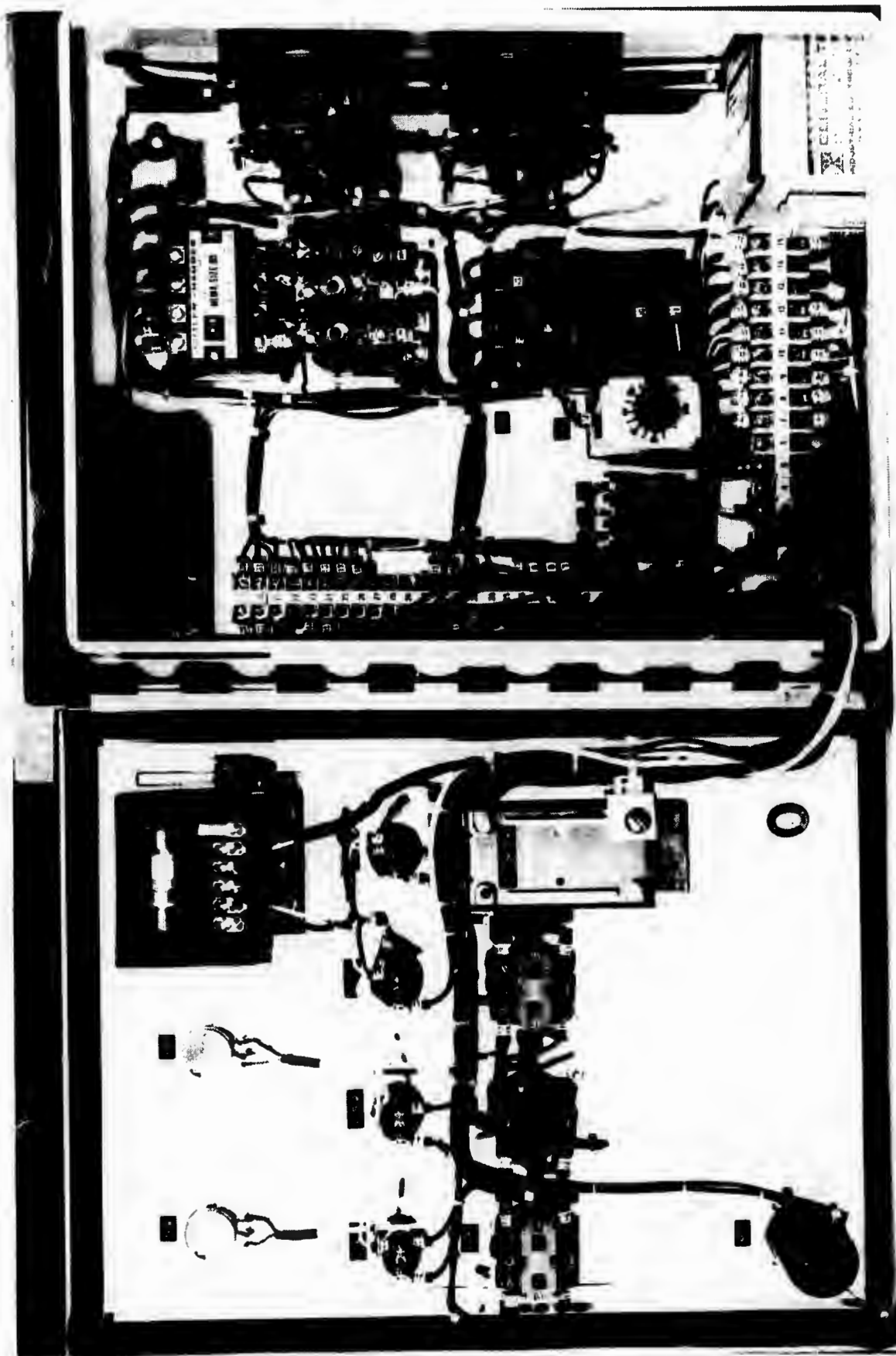


Photo No. 1. Control Cabinet Interior



Photo No. 2. Power Supply

Engelhard Power Supply (cont)

input breaker is rated at 15 amps. The two output breakers are each rated at 200 amps.

Stepdown Transformer and 220V Breakers (Photo No. 3)

Provides the control system with 220V/110V single phase power at 2 KVA.

Two phases of the input 440V, 3 phase, power are coupled to the primary of the stepdown transformer. The 220V center-tapped secondary is fed to a dual 20 amp breaker. From this point, the 220V power is terminated on a barrier strip in the control cabinet. Distribution is made from the barrier strip as necessary.

Most of the switches and other control functions are located in the control cabinet. The power on-off pushbuttons are located on the left-center portion of the panel (see Photograph No. 4). Three other switches to the right of the on-off switch control the feed pump, recirculation pump and sludge pump. Above these switches are indicator lights for each pump. In the upper right corner are two speed control dials, one for the feed pump and the other for the sludge pump. In the upper left corner is a temperature monitor. The thermocouple for this unit is located in the recirculation line.

The power supply is a standard Engelhard saturable reactor unit. Its operation is discussed in Engelhard's "Instruction Manual for Chloropac Electrolytic Sodium Hypochlorite Generator." Chapters III and IV of the manual describe the operational controls and their locations as well as the setup procedures.

The BIF salt feeder has a power hand-off-auto toggle switch and a rate setting feed dial (see Photograph No. 5). The calibration and operation of the salt feed are described elsewhere in this report.



Photo No. 3. System Controls

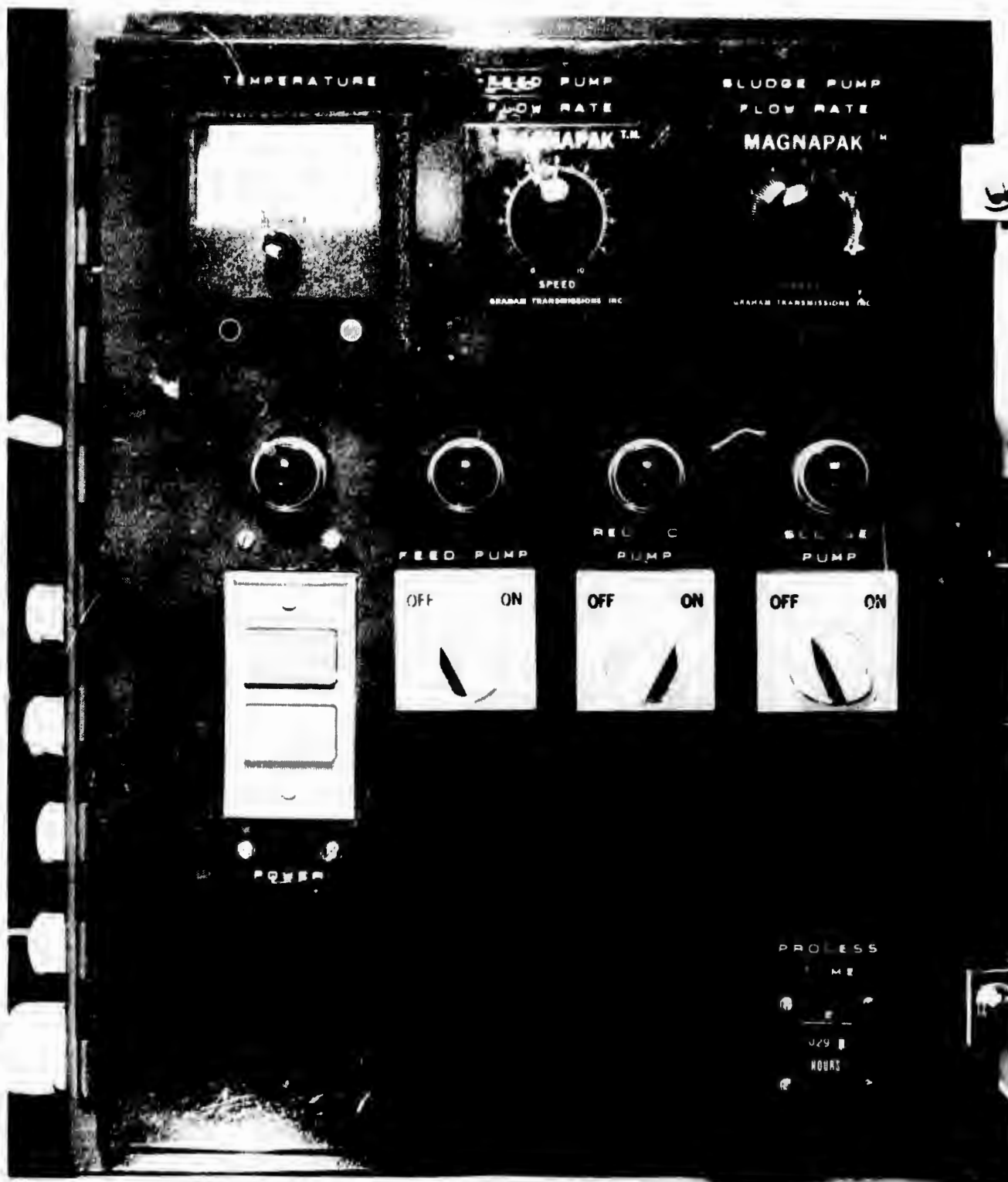


Photo No. 4. Control Panel



Photo No. 5. BIF Feeder Control

The sequence of starting the system is as follows:

1. Close primary duct switch for 440 volt, 3 phase power.
2. Close dual 20 amp breaker on 220 volt single phase (Photo No. 3).
3. Close the input breaker on the Engelhard power supply (Photo No. 6).
4. Close the two output breakers (220 amp) on the Engelhard power supply (Photo No. 6).
5. Push the "on" button on the control cabinet to turn power on.
6. Turn recirculation pump switch to on. Contacts on the recirculation pump starter will allow the power supply to put out full power. If flow in the recirculation loop becomes normal, the system continues to operate. Should flow be inadequate, the power latching relay will be dropped after a preset time delay. This will terminate power to the whole system. After correction of the flow problem, power can be restarted.
7. Assuming normal flow conditions, the feed pump switch is turned on.
8. If, during the operation of the system, the cell voltage exceeds + 15 VDC, the power will again be dropped after a preset time delay. After an overvoltage condition, it will be necessary to depress the overvoltage reset pushbutton on the power supply.
9. Turning the system off can be accomplished by pushing the power off button.

Settling Tank

The settling tank is a rectangular vessel having a capacity of 140 gallons with a hopper bottom for accumulation of sludge. The tank is coated with a vinyl ester film for corrosion protection. It contains a flow distribution baffle and an overflow weir.

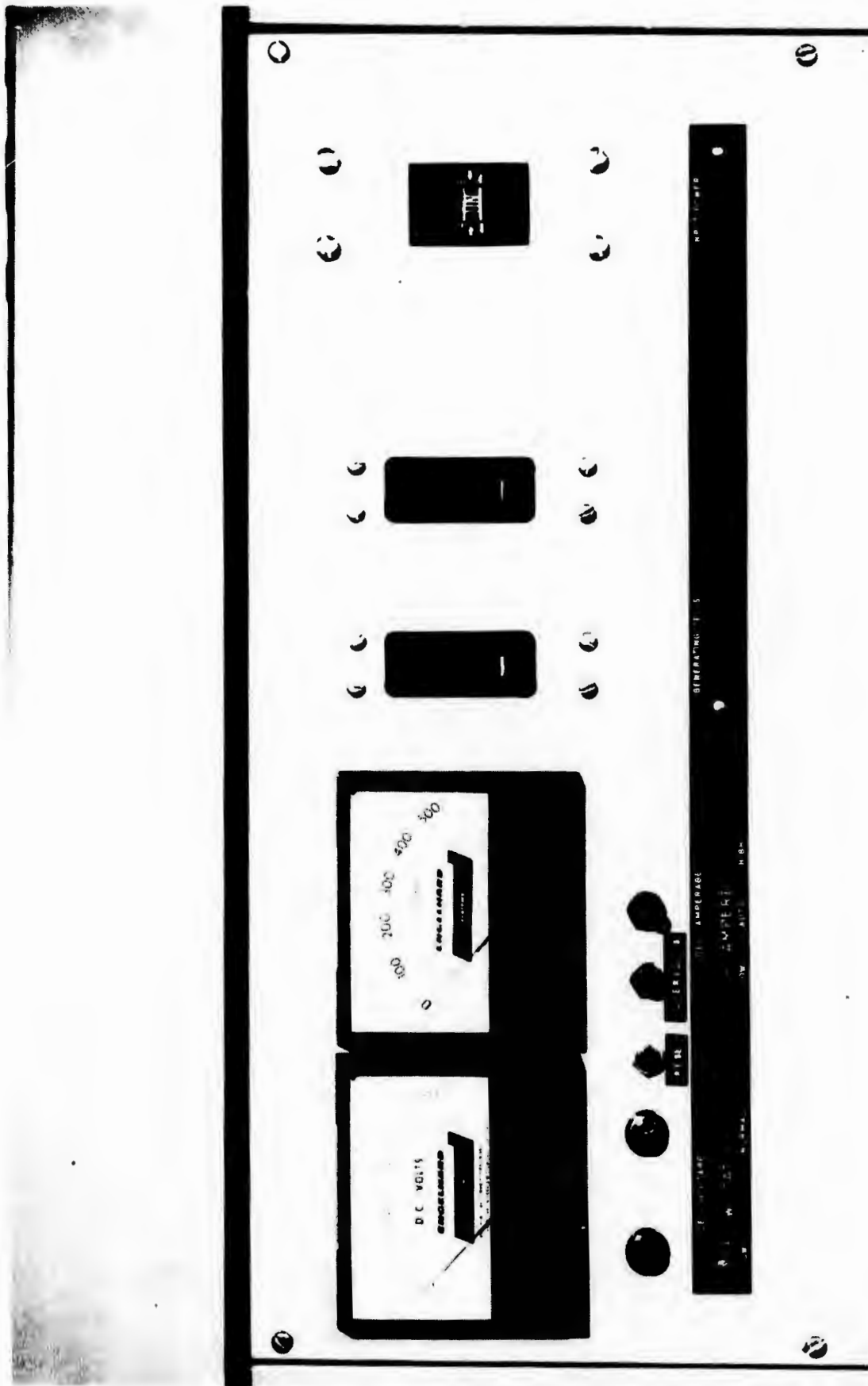


Photo No. 6. Power Supply Controls

Settling rate tests were conducted to support the design of the settling tank. A six-inch diameter column, six feet tall, was constructed with sample taps located at one foot intervals. Solutions of copper cyanide were treated with sodium hypochlorite to produce a suspension of copper hydroxide. The resulting suspension was allowed to settle in the column and samples were withdrawn periodically for suspended solids analysis. Test solutions containing 285 and 518 mg/l CN^- concentrations were evaluated. Data obtained from these tests are presented in Table 7. A graphical interpretation of these data relating suspended solids remaining in suspension with settling velocity and overflow rate is presented in Figure 10. From this figure, an overflow rate of 250 gal/day-sq ft was selected for the settling tank design. This is equivalent to three sq ft of ideal settling area for the design process rate of 0.5 gpm (720 gal/day). An additional five sq ft of cross section was added for entrance and exit zones resulting in a total cross sectional area of eight sq ft. A detailed sketch of the settling tank is presented in Figure 11.

Sludge Pump

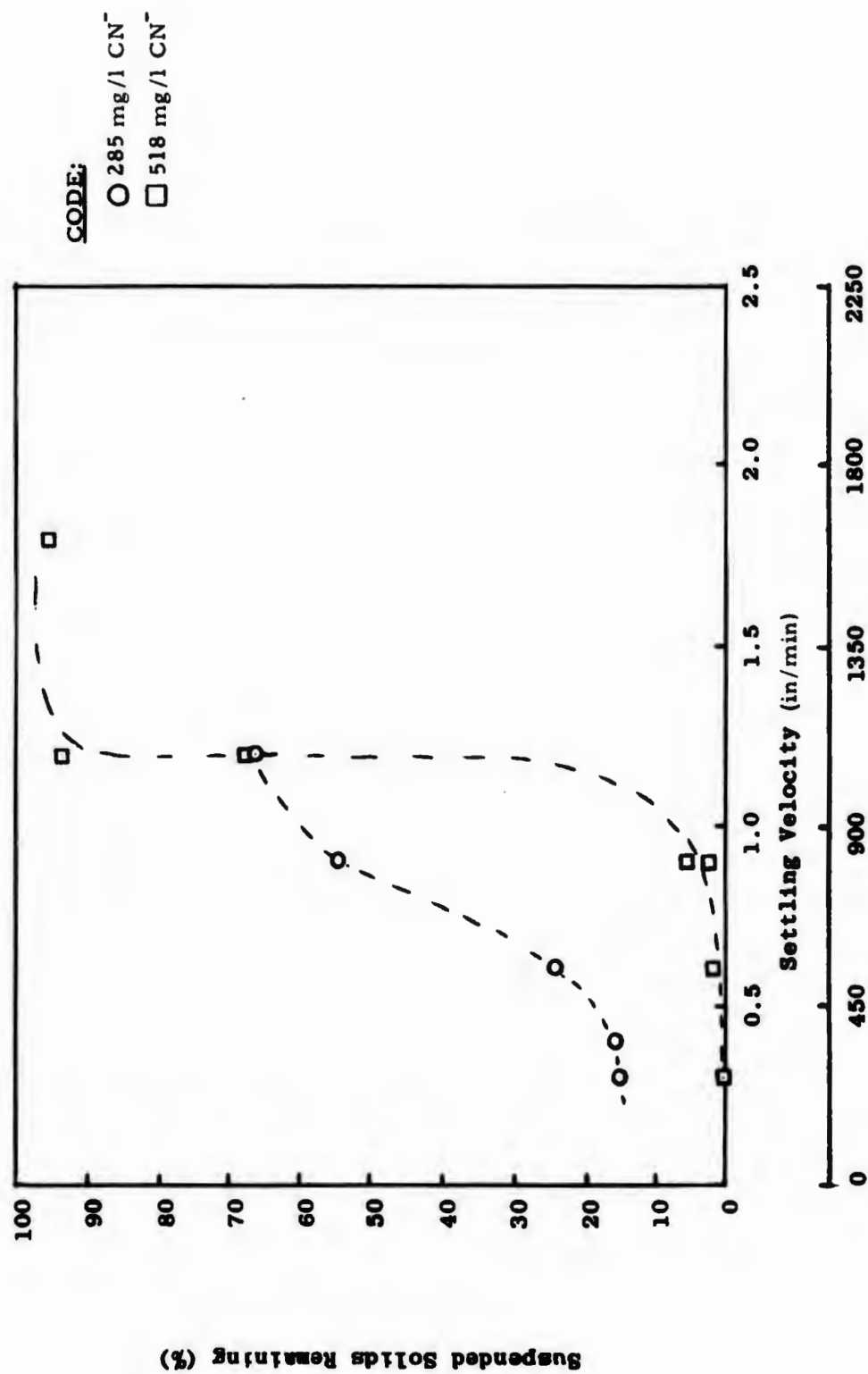
The sludge pump is a progressive cavity, positive displacement pump, Model BA-100, manufactured by the Moyno Pump Division of Robbins & Myers, Inc. It is driven by an SCR controlled, variable speed dc-motor. The displacement of the pump is 0.073 gal/100 revolutions at a discharge pressure of 10 psig.

Ventilation

Hydrogen gas is formed through electrolysis of the water at the cathode of the electrolytic cells and is vented into the chlorination tank. Hydrogen is a highly flammable gas and forms an explosive mixture with air (LEL = 4.1%, UEL = 74.2%). The theoretical hydrogen evolution rate is calculated as 2.44×10^{-4} scfm/amp.

TABLE 7
SETTLING RATE DATA
COPPER HYDROXIDE

CN- Conc (mg/l)	Depth (inches)	Time (min)	Suspended Solids (mg/l)	Settling Velocity (inches/min)	Susp. Solids Remaining (%)
285	18	0	322	-	100
285		15	212	1.2	66
285		20	174	0.9	54
285		30	76	0.6	24
285		45	50	0.4	16
285		60	48	0.3	15
285	54	0	322	-	100
285		15	218	3.6	68
285		20	178	2.7	55
285		30	156	1.8	48
285		45	68	1.2	21
285		60	52	0.9	16
518	18	0	810	-	100
518		15	542	1.2	67
518		20	39	0.9	5
518		30	16	0.6	2
518		60	3	0.3	0.4
518	54	0	810	-	100
518		30	771	1.8	95
518		45	751	1.2	93
518		60	13	0.9	2



Overflow Rate (gal/day - sq. ft.)

Figure 10. Settling Rate Characteristics Copper Hydroxide

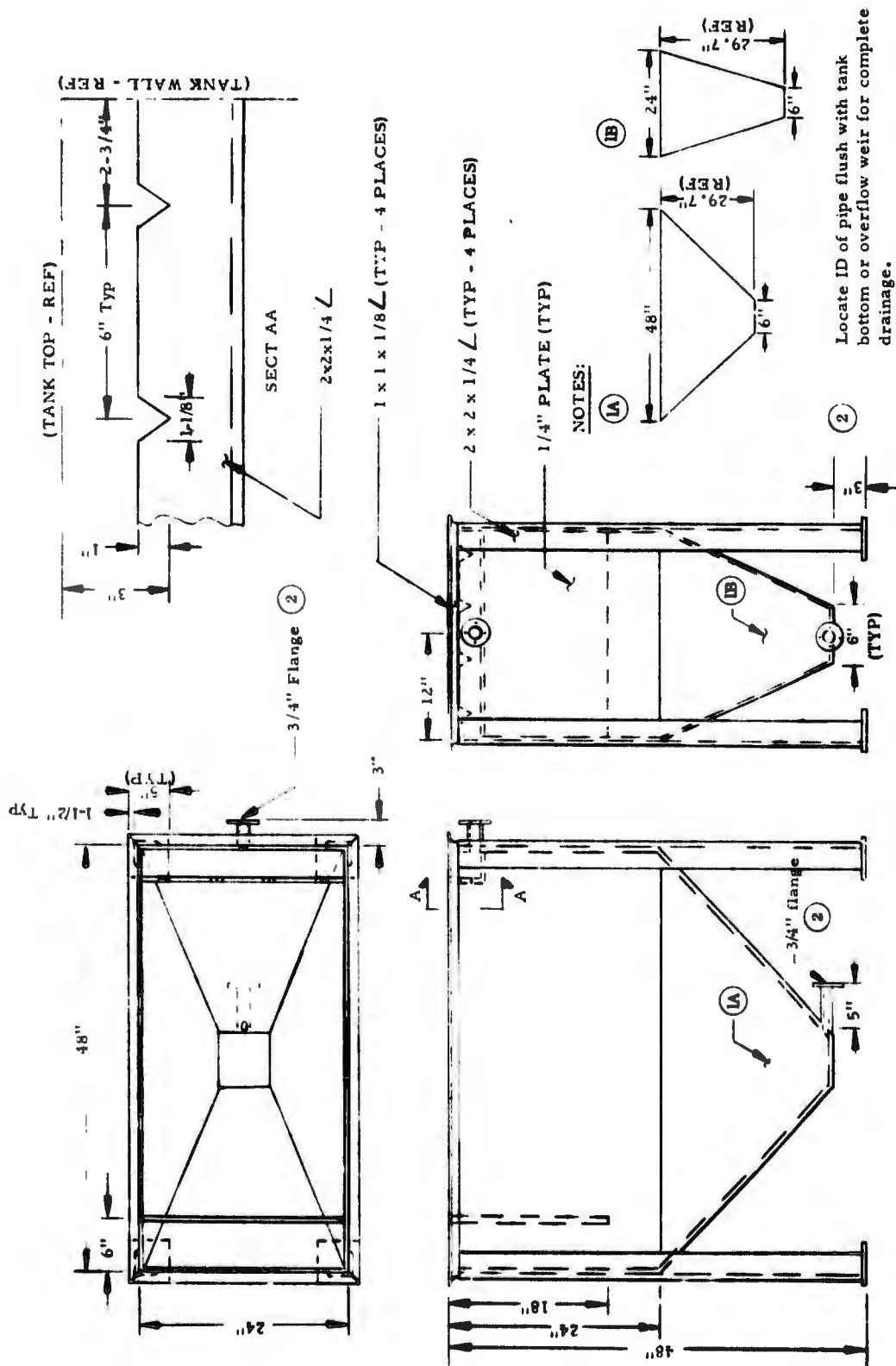


Figure 11. Settling Tank Cyanide Treatment Prototype

At full system power, a current of 400 amps is delivered to the two Chloropac cells. Since the cells are connected electrically in a series-parallel configuration, this is equivalent to an electrolysis current of 800 amps. As indicated in Figure 12, this current will evolve 0.195 Ccfm of hydrogen gas. A ventilation rate in excess of 5 scfm is required to avoid an explosive air-hydrogen mixture. A forced draft ventilation system is used to provide an adequate ventilation rate.

CALIBRATION OF COMPONENTS

In order to insure proper functioning of critical components, calibration and performance verification tests were conducted.

Process Pump

The process pump is a progressive cavity, positive displacement pump, Model BA-100, manufactured by the Moyno Pump Division of Robbins & Myers, Inc. It is driven by an SCR controlled, variable speed dc-motor. The feed tank was charged with a dilute cadmium strip solution of approximately 400 mg/l CN^- concentration. The pump was operated at several rotational speeds as determined by the SCR speed control settings. The liquid delivered during measured time periods was collected and the delivery rates were calculated. The data accumulated during these tests are presented in Table 8. The pump delivery rate is plotted as a function of motor speed control setting in Figure 13. A speed control setting of 0.5 will produce the required process flow rate of 0.5 gpm.

Salt Feeder

A BIF volumetric solids feeder, Model 25-04, with a 0.75 inch diameter helix and helix rotational speed of 10.5 rpm is used to deliver salt to the cyanide destruct unit. The feeder was charged with granulated salt and operated at rate settings of 25, 50, 75, and 100 percent. The salt delivered at these settings during measured time periods was collected and

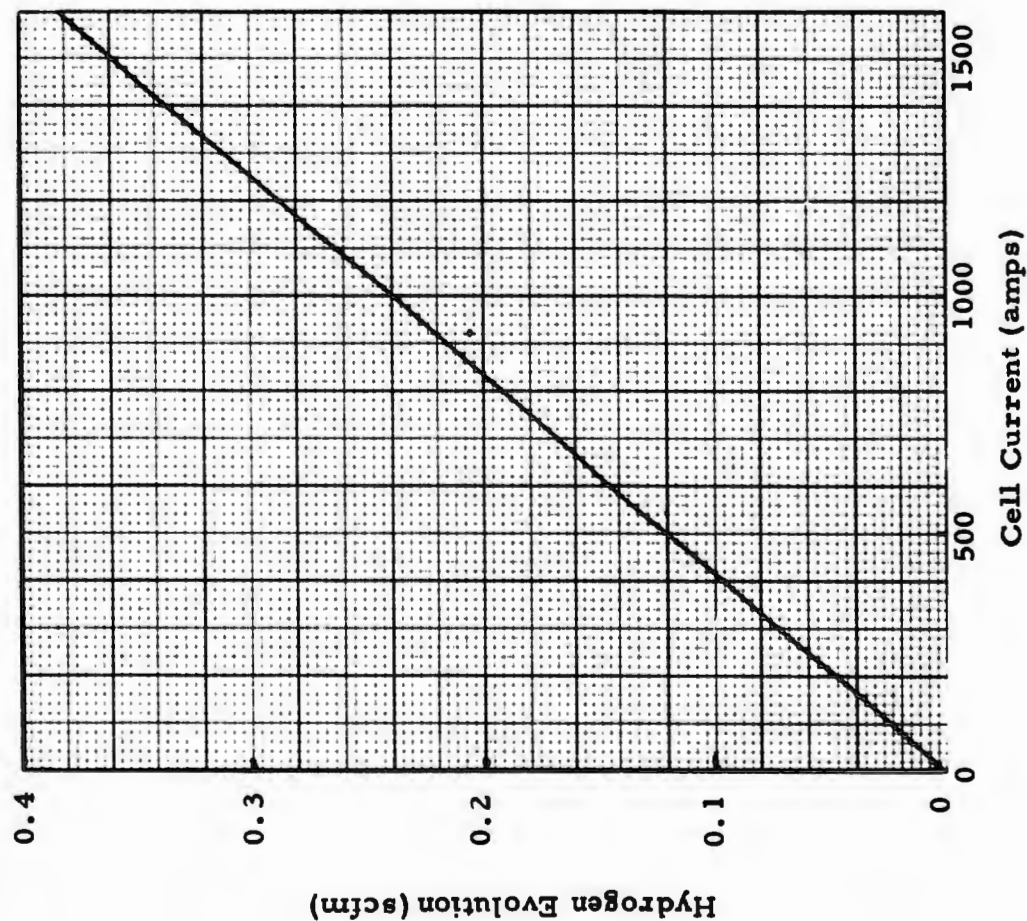
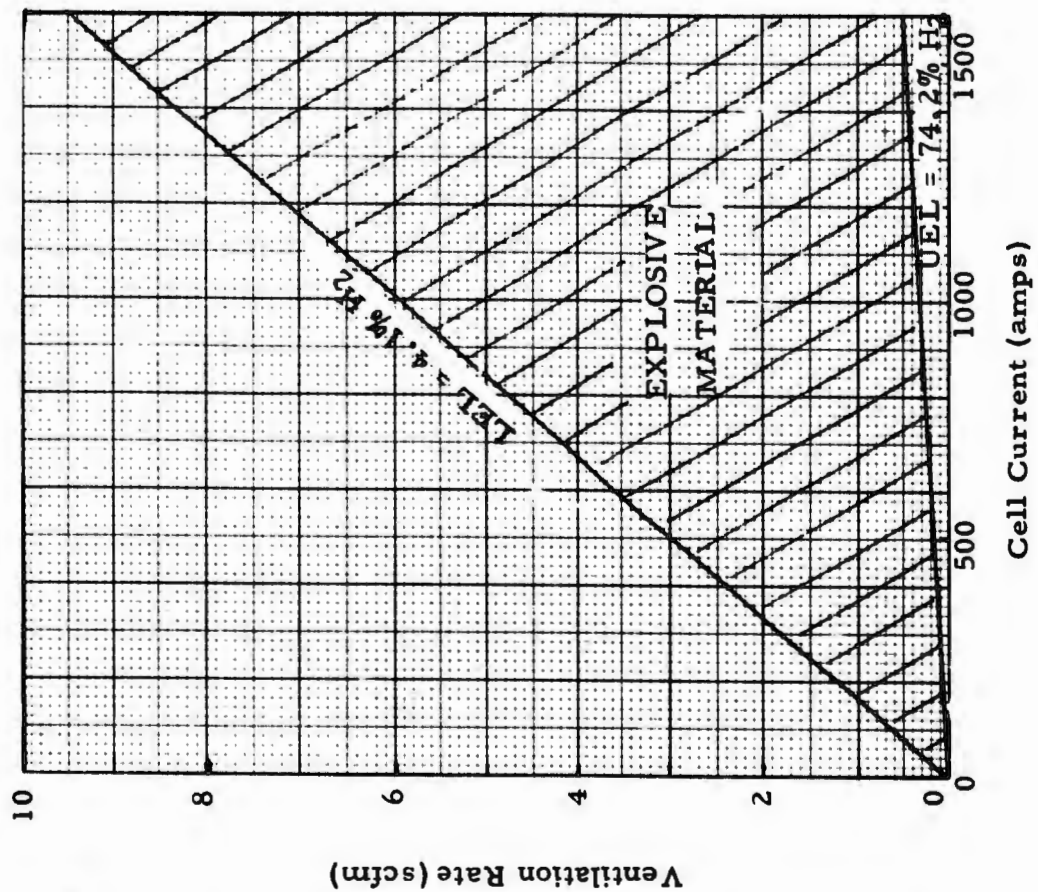


Figure 12. Hydrogen Gas Evolution and Gas Ventilation Rate vs Cell Current

TABLE 8
CALIBRATION OF PROGRESSIVE CAVITY PUMP
MOYNO BA-100

<u>Motor Speed Control Setting</u>	<u>Volume Delivered</u>	
	<u>(ml/min)</u>	<u>(gal/min)</u>
0.43	1100	0.290
0.50	1850	0.489
0.57	2600	0.687
0.63	3200	0.845
0.415	1050	0.277
0.485	1900	0.502
0.56	2500	0.661

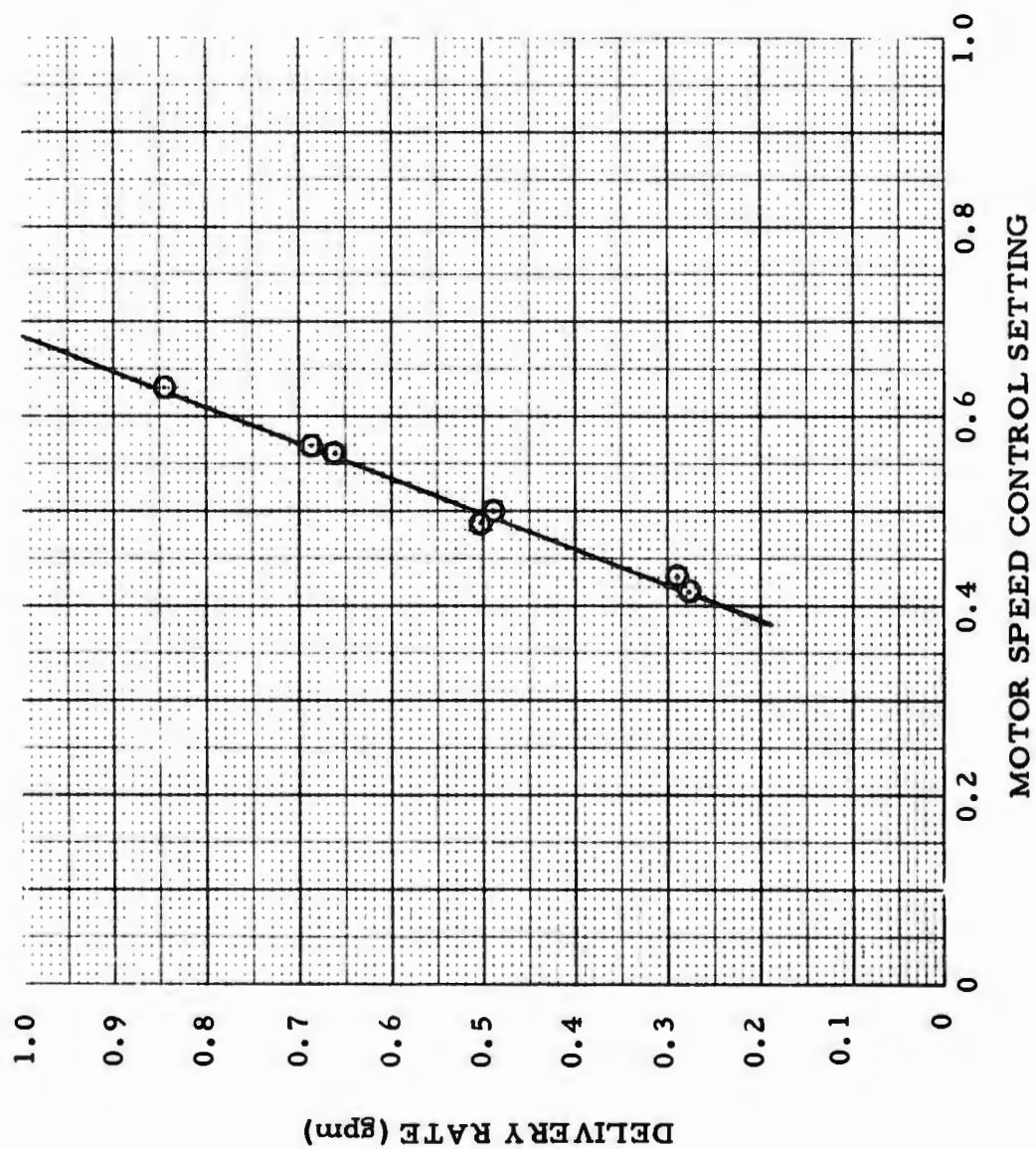


Figure 13. Calibration of Progressive Cavity Pump Moyno BA-100

weighed. The data obtained during these tests are presented in Table 9. The salt delivery rate is plotted as a function of feeder rate setting in Figure 14. The required salt delivery rate of 5 lb/hour is achieved at a rate setting of 90 percent.

Electrolytic Cells

The cyanide destruct system contains two Chloropac cells (four half cells) arranged hydraulically in series flow and connected electrically in a series-parallel arrangement as shown in Figure 15. The cells were calibrated for chlorine generating capacity under simulated operation conditions of flow, temperature, and salinity. Salt water was recycled through the cells from a recycle tank at a flow rate of approximately 19 gpm. A constant net flow of 0.5 gpm of process liquid (plant water) was maintained through the system. The salt concentration was maintained by the BIF volumetric feeder. Salt concentrations of one, two, and three percent were tested with cell currents of 100, 200, 300, and 400 amps.* The chlorine concentration of the effluent was monitored using a Model CN-21-P Hach Kit (potassium iodide, sulfamic acid, phenylarsine oxide). Equilibrium data obtained from these tests are presented in Table 10. The relationship of chlorine concentration, flow rate, and effective current** at salt concentrations of one, two, and three percent is presented graphically in Figure 16. It is observed that cell efficiency

*The 300 and 400 amp tests at one percent salt water concentration were omitted because of high cell voltages required. Cell potentials in excess of nine volts will result in anode damage.

**The effective current available for electrolysis is 200 percent of the applied current due to the series-parallel electrical arrangement of the cells.

TABLE 9
 CALIBRATION OF BIF MODEL 25-04 CHEMICAL FEEDER
 Helix Diameter = 0.75 inches
 Helix Rotation = 10.5 rpm

<u>Rate Setting (%)</u>	<u>Run Time (minutes)</u>	<u>Salt Delivered (grams)</u>	<u>Salt Delivery Rate (grams/min)</u>	<u>(pounds/hour)</u>
25	15	146	9.7	1.29
50	15	301	20.0	2.65
75	15	486	32.4	4.29
100	15	628	41.9	5.54

Helix Diameter: 0.75 Inches
Helix Rotation: 10.5 RPM

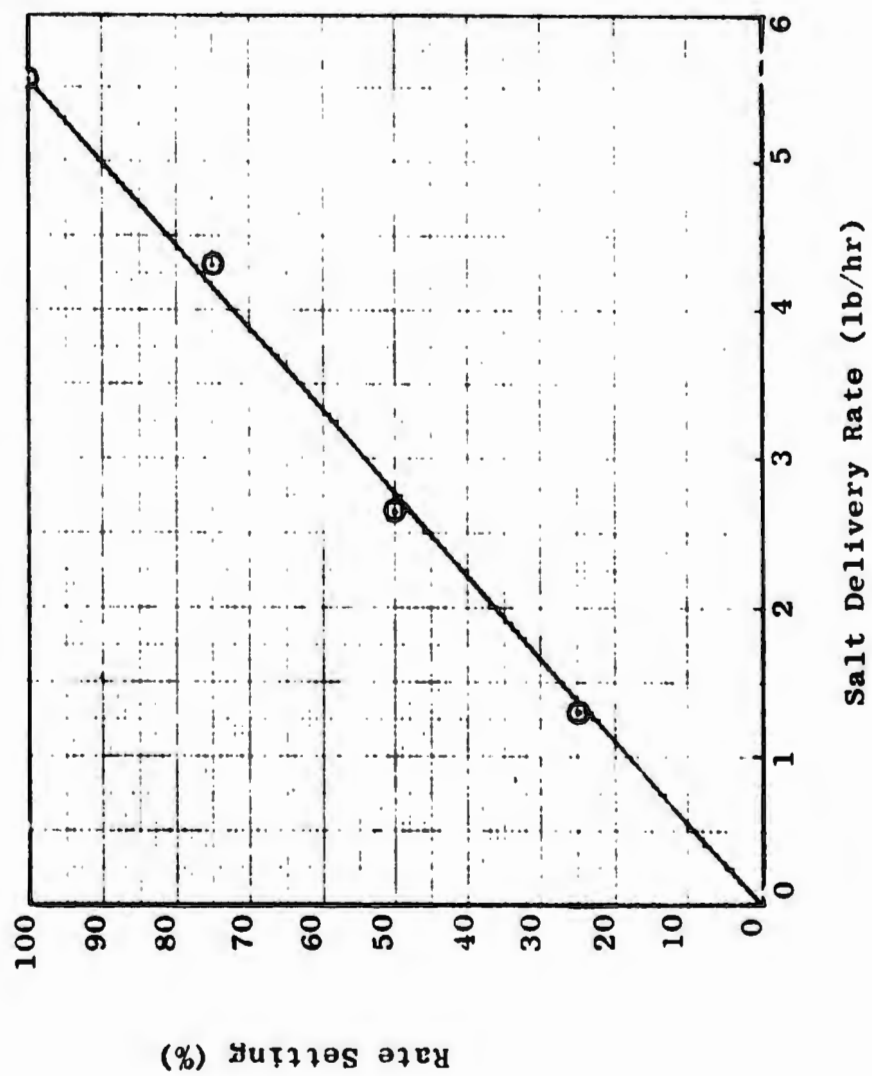


Figure 14. Calibration of BIF Model 25-04 Chemical Feeder

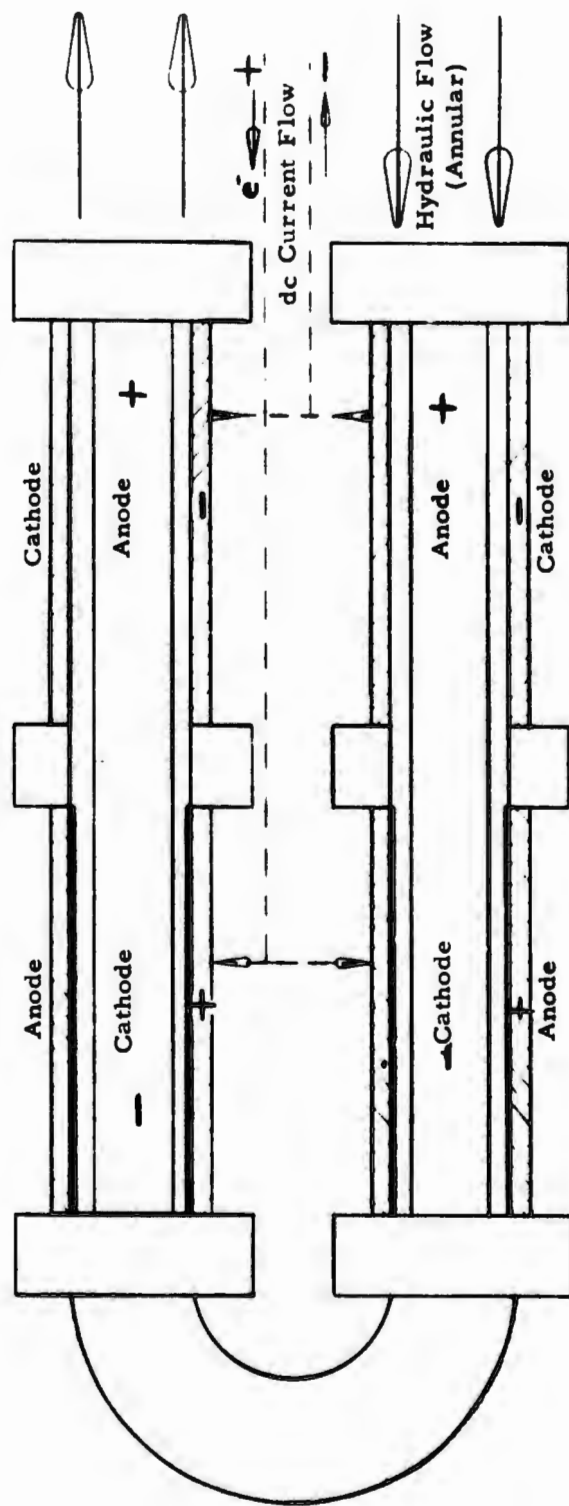


Figure 15. Schematic of Electrolytic Cell Showing Electric and Hydraulic Flow Paths

TABLE 10
CALIBRATION OF ENGELHARD
ELECTROLYTIC CELLS

<u>Flow Rate (gpm)</u>		<u>Power Supply</u>		<u>Salt Conc. (%)</u>	<u>Temp (°F)</u>	<u>pH</u>	<u>Chlorine (mg/l)</u>
<u>Feed</u>	<u>Recycle</u>	<u>(amps*)</u>	<u>(volts)</u>				
0.5	19	100	11.4	1	63	8.9	1100
0.5	19	200	14.8	1	78	8.8	2200
0.5	19	100	9.5	2	67	8.8	1700
0.5	19	200	11.2	2	69	8.8	3000
0.5	19	300	12.4	2	81	8.8	3800
0.5	19	400	13.3	2	91	9.1	4600
0.5	19	100	9.0	3	61	9.0	1800
0.5	19	200	10.5	3	68	9.0	3150
0.5	19	300	11.4	3	75	9.0	4600
0.5	19	400	11.3	3	90	9.2	5800

* Amperage applied to four cells connected in series-parallel.

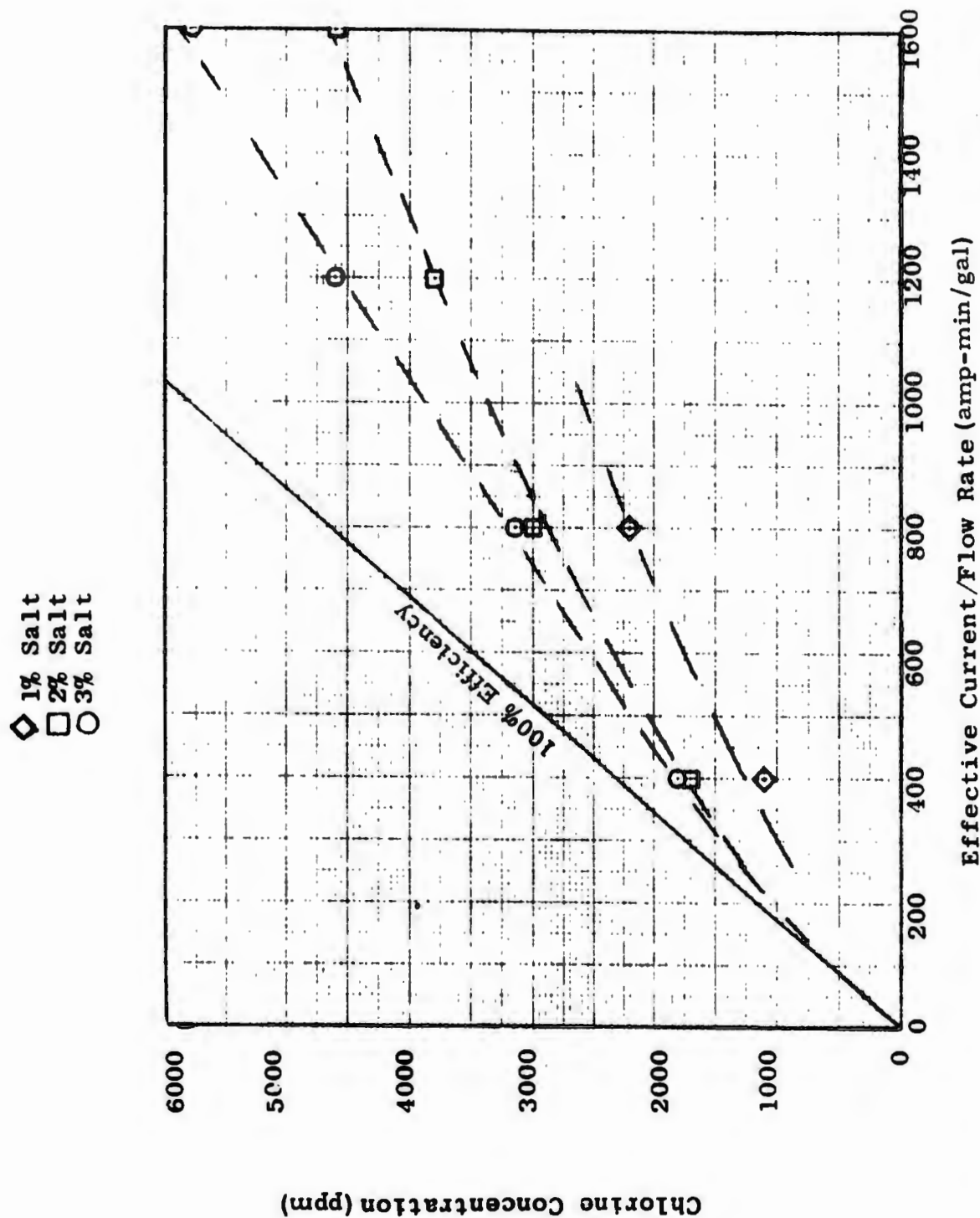


Figure 16. Calibration of Engelhard Electrolytic Cell Capacity = 50 lb Chlorine/Day

decreases as the salt concentration is reduced, as the process temperature is increased and as the ratio of chlorine to available chloride (conversion) is increased. The amount of chlorine generated under design conditions of two percent salt concentration and a process temperature of 90-100°F was 4600 mg/l. Assuming a process liquid density of 8.3 lb/gal, this is equivalent to a chlorine production rate of 27.5 lb chlorine per day. This agrees with the output of 14 lb chlorine per day per cell (28 lb chlorine per day total) assumed in the system design. It is slightly deficient of the 30 lb chlorine per day requirement established as the peak system chlorine demand, however. The addition of a third cell to increase the chlorine output in excess of 30 lb chlorine per day was not deemed necessary.

SYSTEM OPERATION

The prototype cyanide destruct system was tested using dilute solutions of cadmium strip, nickel strip, copper plate, and cadmium plate wastewater obtained from Air Force plating facilities. The results of these test runs are presented in Tables 11 through 14. The range of influent and effluent cyanide concentrations experienced were:

	Influent CN ⁻ Conc (mg/l)	Effluent CN ⁻ Conc (mg/l)	
		May, Jun, Jul	Jun, Jul
Cadmium Strip	13.75-462	0.036- 2.75	0.036- 0.363
Nickel Strip	1.25-161.25	0.17 - 0.64	0.17 - 0.64
Copper Plate	6.25-483.7	0.029- 0.945	0.13 - 0.21
Cadmium Plate	56.25-632.5	8.75 -25.8	8.75 -25.8

Effluent data obtained during May are suspect because of variations found in the analytical technique as discussed in Section II. June and July data are considered to be more accurate and are observed to be more consistent than the May data indicating improved precision of analysis.

TABLE 11
CYANIDE TREATMENT PROTOTYPE PERFORMANCE
CADMIUM STRIP SOLUTION

Date	Feed Rate (gpm)	Salt Conc (%)	Power Supply (amps)	Power Supply (volts)	Influent				Effluent				
					CN (mg/l)	CNO (mg/l)	Temp (°F)	pH	CN (mg/l)	CNO (mg/l)	Temp (°F)	pH	Chlorine (mg/l)
6 May 74	0.5	2	400	12.1	308.6	138	-	-	0.084	4.6	103	7.3	160
7 May 74	0.5	2	400	12.3	411.9	168	-	-	0.097	3.4	104	7.3	160
16 May 74	0.5	2	400	12.6	378.8	216.8	60	10.3	0.54	85.7	96	7.4	130
20 May 74	0.5	2	400	12.4	357.5	109	60	10.3	0.32	4.0	96	7.2	150
22 May 74	0.5	2	400	12.1	363.8	165	-	-	0.13	4.0	99	7.2	150
23 May 74	0.5	2	400	12.2	320	130	-	-	0.30	13.0	98	7.3	90
28 May 74	0.5	2	400	12.0	322.8	117.7	-	-	0.86	10.5	108	7.3	120
29 May 74	0.5	2	400	12.0	394.4	151.3	45	10.3	0.37	14.7	105	7.3	100
18 Jun 74	0.5	2	400	11.7	462	100.8	76	-	0.363	8.4	112	7.6	70
19 Jun 74	0.5	2	200	9.9	243.75	84.04	70	10.5	0.275	6.3	89	-	60
19 Jun 74	0.5	2	120	9.0	116.25	16.8	70	10.2	0.27	4.2	82	7.7	80
20 Jun 74	0.5	2	60	8.1	57.25	42.02	70	7.8	0.19	10.5	74	7.8	90
20 Jun 74	0.5	2	35	7.5	30.0	33.6	-	-	0.15	2.1	72	-	60
21 Jun 74	0.5	2	15	7.0	13.75	21.01	-	-	0.036	6.3	70	8.0	50

TABLE 12
CYANIDE TREATMENT PROTOTYPE PERFORMANCE
NICKEL STRIP SOLUTION

Date	Feed Rate (gpm)	Salt Conc (%)	Power Supply (amps)	Power Supply (volts)	Influent				Effluent				Chlorine (mg/l)
					CN ⁻ (mg/l)	CNO ⁻ (mg/l)	Temp (°F)	pH	CN ⁻ (mg/l)	CNO ⁻ (mg/l)	Temp (°F)	pH	
1 July	0.5	2	400	10.5	161.25	79.8	71	10.3	0.64	35.7	103	8.0	40
1 July	0.5	2	200	9.0	43.75	27.3	-	-	0.27	8.4	88	7.7	140
2 July	0.5	2	70	7.2	7.5	8.4	69	8.8	0.17	2.1	75	8.0	90
2 July	0.5	2	35	6.5	1.25	6.3	-	7.9	0.19	2.1	73	8.2	90

TABLE 13
CYANIDE TREATMENT PROTOTYPE PERFORMANCE
COPPER CYANIDE SOLUTION

Date	Feed Rate (gpm)	Salt Conc (%)	Power Supply		Influent				Effluent				
			(amps)	(volts)	CN (mg/l)	CNO (mg/l)	Temp (°F)	pH	CN (mg/l)	CNO (mg/l)	Temp (°F)	pH	Chlorine (mg/l)
8 May 74	0.5	2	400	12.4	306.8	81	67	9.7	0.50	9.2	98	7.6	320
									0.13	8.4	100	7.7	400
14 May 74	0.5	2	400	12.9	483.7	205.2	58	9.8	0.945	28.6	94	7.6	120
14 May 74	0.5	2	200	10.6	258.7	169.7	60	9.5	0.445	13.4	77	7.3	100
15 May 74	0.5	2	100	9.0	210.0	145.9	60	8.8	0.029	52.1	66	7.5	240
21 Jun 74	0.5	2	400	12.0	318.75	134.5	-	-	0.13	12.6	100	-	380
25 Jun 74	0.5	2	100	8.5	102.5	2.1	70	9.4	0.19	14.7	75	7.6	130
25 Jun 74	0.5	2	25	7.0	35	10.5	-	-	0.19	4.2	76	7.6	90
26 Jun 74	0.5	2	10	6.7	6.25	18.9	-	-	0.21	12.6	68	8.0	100

TABLE 14
CYANIDE TREATMENT PROTOTYPE PERFORMANCE
CADMIUM PLATE SOLUTION

Date	Feed Rate (gpm)	Salt Conc (%)	Power Supply (amps)	Power Supply (volts)	Influent				Effluent				
					CN ⁻ (mg/l)	CNO ⁻ (mg/l)	Temp (°F)	pH	CN ⁻ (mg/l)	CNO ⁻ (mg/l)	Temp (°F)	pH	Chlorine (mg/l)
27 June	0.5	2	400	11.0	632.5	239.1	-	-	25.8	60.9	95	10.8	30
27 June	0.5	2	350	9.7	132.5	111.4	-	-	16.25	35.7	92	10.6	50
28 June	0.5	2	250	9.3	56.25	14.7	69	10.2	8.75	10.5	85	10.2	140

The system performed satisfactorily on the cadmium strip, nickel strip, and copper plate. Problems were encountered with the cadmium plate solution as indicated by the relatively high effluent cyanide concentrations. The pH of the cadmium plate concentrate was very high and formed a white precipitate (calcium and magnesium carbonates and hydroxides) when diluted with plant water. Abnormally high cell currents were required to maintain residual chlorine in the effluent indicating either a significantly higher chlorine demand or a reduced cell efficiency.

Because of the problems encountered with the cadmium plating waste, a bench scale test was conducted to evaluate the effect of pH on the cyanide-hypochlorite reaction. A one liter sample of the plating waste was prepared using a dilution factor of 50:1. Two 500 ml aliquots were taken for testing. The pH of sample 1 was reduced to 7.6 with hydrochloric acid. The pH of sample 2 was left unchanged at 10.7. Twenty ml of Clorox were added incrementally to each sample. The pH of the samples was reduced to 6.8 and 10.5 respectively as a result of the Clorox addition. The residual chlorine in sample 1 was very high as indicated by starch-iodide test paper. The two treated samples were analyzed for cyanide and cyanate. The results of these tests are presented below:

	<u>CN⁻ Conc (mg/l)</u>	<u>CNO⁻ Conc (mg/l)</u>
Sample 1	5.0	11.25
Sample 2	48.3	90.3

These data indicate that reduced pH conditions improved cyanide reduction. The concentrate was analyzed for heavy metals and the results of these tests are as follows:

<u>Cation</u>	<u>Concentration (mg/l)</u>
Copper	1,347
Silver	445
Iron	256
Nickel	12
Chromium	31

These data indicate a complete lack of cadmium ion. Therefore, the solution processed in the prototype was not considered a normal cadmium plating solution. The high iron content, if complexed with the cyanide present, would contribute to the difficulty in completely oxidizing the cyanide to comparable levels observed with the other plating wastes. No further tests were conducted with this solution.

A settling tank, designed to remove metal hydroxide precipitates formed during the chlorination reaction, was added to the system during the test runs involving copper plating solution, cadmium plating solution, and nickel strip solution. The process flow entering and leaving the settling tank was sampled periodically and the suspended solid concentration was measured. The results of these tests are presented in Table 15. The settling tank performed well with the copper plating solution, producing a very clear effluent. Suspended solids in the effluent on the first day ranged from 28 to 78 mg/l with an influent concentration of 527 mg/l. Liquid from subsequent test runs continued to appear very clear although suspended solids concentrations of 100 to 217 mg/l were reported. The settling tank was not as effective in removing the excessive amounts of carbonate precipitate in the cadmium plate waste stream. Although as much as 90 percent of the precipitate was removed, effluent suspended solids concentrations of 157 to 560 mg/l were reported. The effluent was very turbid.

Preliminary laboratory test data indicated that activated carbon was effective in removing residual traces of cyanide from the effluent. A 1.5 liter column of Barneby Cheney PC-50 activated carbon was added to the prototype

TABLE 15
SETTLING TANK PERFORMANCE

Flow Rate: 0.5 gpm

<u>Date</u>	<u>Feed Solution</u>	<u>Suspended Solids (mg/l)</u>	
		<u>Influent</u>	<u>Effluent</u>
21 June	Copper Plate	527	29*
			28*
			28*
			73*
			78*
25 June	Copper Plate	400	145
	" "	353	217
26 June	Copper Plate	240	100
27 June	Cadmium Plate	2293	243
	" "	2083	560
28 June	Cadmium Plate	1617	157
1 July	Nickel Strip	168	266
	" "	246	266
2 July	Nickel Strip	128	120
	" "	126	120

*Hourly Samples

system as a final treatment stage. Effluent from the prototype was metered through the column at a rate of 0.5 gpm. Samples of the process liquid entering and leaving the column were taken at hourly intervals and composited for analysis. The results of these tests are presented in Table 16. These data indicate a very slight cyanide reduction with nickel strip but no change with copper or cadmium plating waste. The column was removed from the system.

At the conclusion of the test period, the prototype was drained and flushed. The components were assembled on two pallets and secured for transport to Hill AFB, Utah, for field testing.

TABLE 16
ACTIVATED CARBON COLUMN PERFORMANCE

Flow Rate = 0.5 gpm
Carbon Volume = 1.5 liters
Carbon Type = Barneby Cheney PC-50 Water Purification Charcoal

Date	Feed Solution	Influent Conc (mg/l)		Effluent Conc (mg/l)	
		CN ⁺	CNO ⁻	CN ⁺	CNO ⁻
25 June	Copper Plate	0.22	2.1	0.22	2.1
	"	0.19	1.68	0.20	2.1
26 June	Copper Plate	0.17	2.10	0.17	10.5
27 June	Cadmium Plate	6.25	27.3	6.25	27.3
	"	15.00	33.6	15.00	29.4
28 June	Cadmium Plate	12.50	4.2	13.75	4.2
1 July	Nickel Strip	10.0	54.6	7.5	39.9
2 July	Nickel Strip	0.27	6.3	0.16	12.6

SECTION IV

FIELD TESTING

The prototype cyanide destruct system was located in the electroplating facility, Building 505, at Hill AFB, Utah, for a one-month field test. The unit was connected to a central surge tank to which the cyanide contaminated rinse water drained. The system was placed on stream on 2 August 1974 and shut down on 30 August 1974. During this time period, the system was operated on week days during the day shift. The system operated a total of 134.5 hours and processed 4,035 gallons of cyanide contaminated wastewater.

Influent and effluent samples were taken from the system at two hour intervals and analyzed for cyanide and cyanate* concentration. Chlorine, pH, and cell voltage were monitored at half-hour intervals. Cell current was adjusted to provide ample chlorine to meet peak demands. The cell current was set at 25 amps during the first few weeks of testing and subsequently increased to 40 amps. Data obtained during the test period are presented in Table 17. These data are summarized as follows:

	<u>Cyanide Conc (mg/l)</u>		<u>Cyanate Conc (mg/l)</u>	
	<u>Influent</u>	<u>Effluent</u>	<u>Influent</u>	<u>Effluent</u>
Average	8.31	0.008	20.40	5.25
Standard Deviation	10.86	0.010	7.06	4.87
Minimum	0.50	<0.001	12.60	0.84
Maximum	46.88	0.050	37.82	18.90

System performance may be more adequately described by examining the frequency distribution of the effluent cyanide concentrations. These data are arranged in Table 18 in concentration groups of 0.0025 mg/l increments.

It is observed that these data form a truncated population distribution, as illustrated in Figure 17, with a high percentage of data points in the very

*The two hour samples were composited for daily cyanate analysis.

TABLE 17
CYANIDE DESTRUCT SYSTEM PERFORMANCE

Test Site: Hill AFB
Process Rate: 0.5 gpm
Salt Conc.: 2 percent

Date	Time	Power Supply		Chlorine (p.p./l)	pH	Cyanide Conc. (n.g./l)		Cyanide Conc. (n.g./l)	
		Amperes	Volts			Influent	Effluent	Influent	Effluent
8-02-74	0830	200	10	900	8.6	3.10	<0.001	25.2	14.7
	1030	50	8.1	1000	8.5	3.10	<0.001		
	1230	25	7.7	160	-	9.58	<0.001		
	1430		7.7	260	-	10.63	0.030		
8-05-74	0830		7.7	300	-	3.63	<0.001	27.3	8.4
	1030		7.8	320	-	4.84	<0.001		
	1230		7.8	340	-	3.68	<0.001		
	1430		7.8	320	8.1	3.68	<0.001		
8-06-74	0830		7.7	340	8.2	2.63	<0.001	18.91	4.2
	1030		7.7	330	8.1	2.38	<0.001		
	1230		7.8	300	-	35.63	<0.001		
	1430		7.8	260	8.1	16.25	<0.001		
8-07-74	0830		7.7	280	8.2	2.87	0.008	12.60	2.1
	1030		7.8	260	8.4	4.87	0.006		
	1230		7.8	260	8.4	10.63	0.005		
	1430		7.8	240	-	6.25	<0.001		
8-08-74	0830		7.5	300	8.15	3.75	0.015	27.30	18.9
	1030		7.5	280	7.80	28.13	0.019		
	1230		7.5	190	7.90	8.13	<0.002		
	1430		7.5	140	7.80	21.88	0.019		
8-09-74	0830		7.5	160	8.00	3.75	0.005	23.10	10.5
	1030		7.4	240	7.80	3.13	0.002		
	1230		7.3	266	7.80	2.50	0.004		
	1430		7.6	200	7.70	46.88	0.025		
8-12-74	0830	25	7.5	300	8.00	4.31	<0.001	33.62	6.30
	1030		7.5	306	7.80	2.50	0.013		
	1230		7.5	320	7.80	3.13	0.011		
	1430		7.5	260	7.60	3.75	0.003		
8-13-74	0830		7.7	260	7.85	3.13	0.007	14.71	2.10
	1030		7.7	180	7.65	0.88	0.003		
	1230		8.0	120	7.80	20.63	<0.002		
	1430		7.7	240	7.70	11.87	0.013		
8-14-74	0830		7.5	300	8.00	2.50	0.004	18.91	4.20
	1030		7.5	280	7.85	5.00	0.011		
	1230		8.0	240	7.90	5.63	0.001		
	1430		8.0	280	7.95	1.38	0.017		
8-15-74	0830		7.7	280	8.10	2.50	0.011	25.21	8.40
	1030		8.0	280	7.90	2.50	0.012		
	1230		8.0	280	7.80	1.38	0.005		
	1430		8.8	220	7.90	15.63	0.014		
8-16-74	0830	50	8.7	360	8.10	3.13	0.011	37.82	2.10
	1030		7.7	290	7.90	3.13	0.018		
	1230		8.0	280	7.85	2.44	0.004		
	1430		8.0	260	7.80	2.00	0.050		
8-17-74	0830		7.7	250	8.05	1.25	0.004	19.96	6.30
	1030		8.0	260	7.85	4.25	<0.002		
	1230		8.0	200	7.70	5.70	<0.002		
	1430		8.0	180	7.90	5.92	0.005		
8-18-74	0830								
	1030								
	1230								
	1430								
SYSTEM NOT OPERATED									
8-21-74	0830	30	8.0	260	8.10	1.50	0.008	15.96	2.52
	1030		8.0	290	8.05	0.90	<0.002		
	1230		8.6	260	7.95	3.50	<0.002		
	1430		8.0	280	8.00	1.30	<0.002		
8-22-74	0830		8.0	260	8.10	1.10	<0.001	17.64	1.68
	1030		8.2	280	8.00	42.50	<0.002		
	1230	50	9.0	210	8.10	17.70	0.006		
	1430	50	8.2	140	8.25	11.90	0.011		
8-23-74	0830		8.2	250	8.10	1.90	0.016	13.45	0.84
	1030		8.2	200	8.80	21.30	0.025		
	1230		8.3	240	8.00	6.10	0.014		
	1430		8.3	300	8.05	2.30	0.032		
8-24-74	0830	50	8.4	330	8.20	0.50	0.018	17.65	4.20
	1030		8.5	380	8.10	2.30	0.015		
	1230		8.5	540	8.10	-	-		
	1430		8.5	600	8.10	3.10	0.010		
8-27-74	0830	40	8.2	510	8.10	0.90	<0.002	13.25	0.84
	1030		8.5	450	7.90	1.10	<0.002		
	1230		8.5	390	7.90	2.90	<0.002		
	1430		8.5	360	7.80	1.40	0.009		
8-28-74	0830		8.5	360	7.90	1.70	0.008	16.88	4.20
	1030		8.5	390	7.90	1.60	<0.002		
	1230		8.5	380	7.95	1.20	<0.002		
	1430		8.5	380	7.90	0.80	0.012		
8-29-74	0830		8.5	390	8.00	2.30	<0.002	15.13	1.68
	1030		8.5	400	7.90	27.70	0.002		
	1230		8.5	300	7.90	28.30	0.028		
	1430		8.6	280	7.90	10.30	0.024		
8-30-74	0830	38	8.4	320	8.10	1.70	0.019	13.45	0.840
	1030	38	8.7	400	8.00	1.30	0.010		
AVERAGE						8.31	0.008	20.40	5.25
STANDARD DEVIATION						10.86	0.010	7.06	4.87
RANGE - MINIMUM						0.50	<0.001	12.60	0.84
RANGE - MAXIMUM						46.88	0.050	37.82	18.90

TABLE 18
CUMULATIVE FREQUENCY DISTRIBUTION
EFFLUENT CYANIDE CONCENTRATIONS

<u>Upper Group Limit (mg/l)</u>	<u>Number of Observations</u>	<u>Cumulative Frequency (%)</u>
0.0025	30	38.96
0.0050	7	48.05
0.0075	8	58.44
0.0100	4	63.63
0.0125	7	72.73
0.0150	4	77.92
0.0175	6	85.71
0.0200	5	92.21
0.0225	0	92.21
0.0250	1	93.51
0.0275	1	94.81
0.0300	1	96.10
0.0325	2	98.70
0.0350	0	
0.0375	0	
0.0400	0	
0.0425	0	
0.0450	0	
0.0475	0	
0.0500	0	
0.0525	<u>1</u>	
		100.00
TOTAL	77	

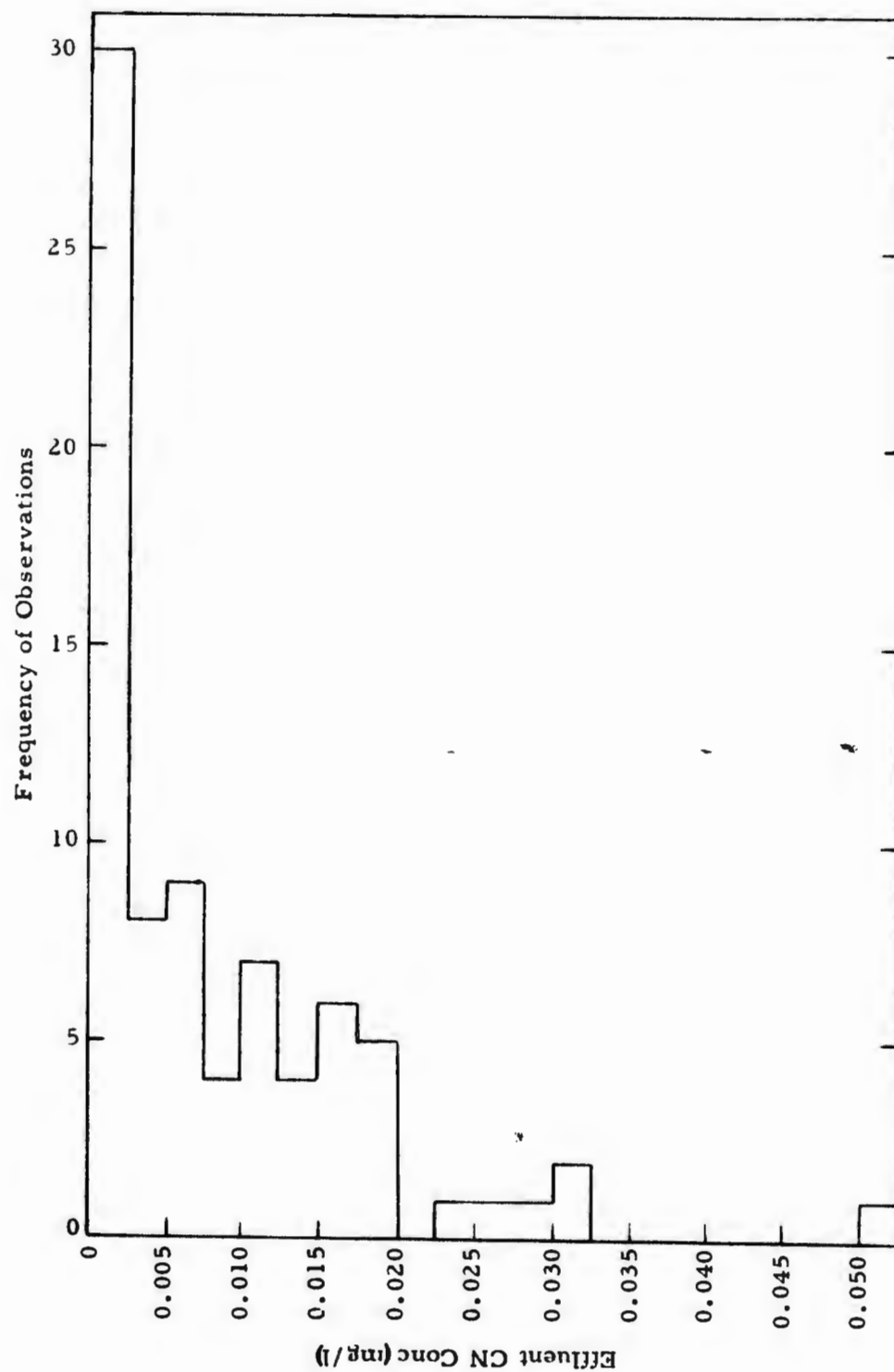


Figure 17. Grouped Frequency Distribution Effluent Cyanide Concentration

low concentration ranges. Examination of these data on probability coordinates, Figure 18, indicates a population mean (50% cumulative frequency) of 0.0045 mg/l and a population mean plus one standard deviation (80.1% cumulative frequency) of 0.0145 mg/l. The population mean (0.0045 mg/l) is a better indication of true system performance than the arithmetic mean (0.008 mg/l) because of the truncated data distribution.

When compared to the state standards for the discharge of cyanide-bearing wastewater, the effluent from the Thiokol system satisfies practically all requirements. Most states require cyanide removal in the range of 0.25 mg/l. The maximum concentration in the system effluent measured during the field tests was 0.050 mg/l, and 94% of the observations showed concentrations less than 0.02 mg/l (Figure 18).

All of these values are below the detectable limit of all laboratories that do not have the photometric equipment for colorimetric analysis. The limit of sensitivity of the standard titration method (modified Liebig) is approximately 0.1 mg/l CN, but at this point the color change is indistinct.

Even with the colorimetric method using a spectrophotometer or filter photometer, the analytical precision one can obtain using the standard method is limited because of the effect of the variables outlined in this report. Only with the special emphasis on analytical techniques used in this program could these cyanide concentration values be confidently reported.

Also during the field testing at Hill AFB, samples were taken periodically to monitor total dissolved solids (TDS), carbonate, bicarbonate, chlorate, and heavy metal concentrations. This information is summarized in Table 19. The TDS, carbonate, bicarbonate, and chlorate were analyzed using standard wet chemical procedures. The heavy metals content was ascertained using emission spectroscopy techniques.

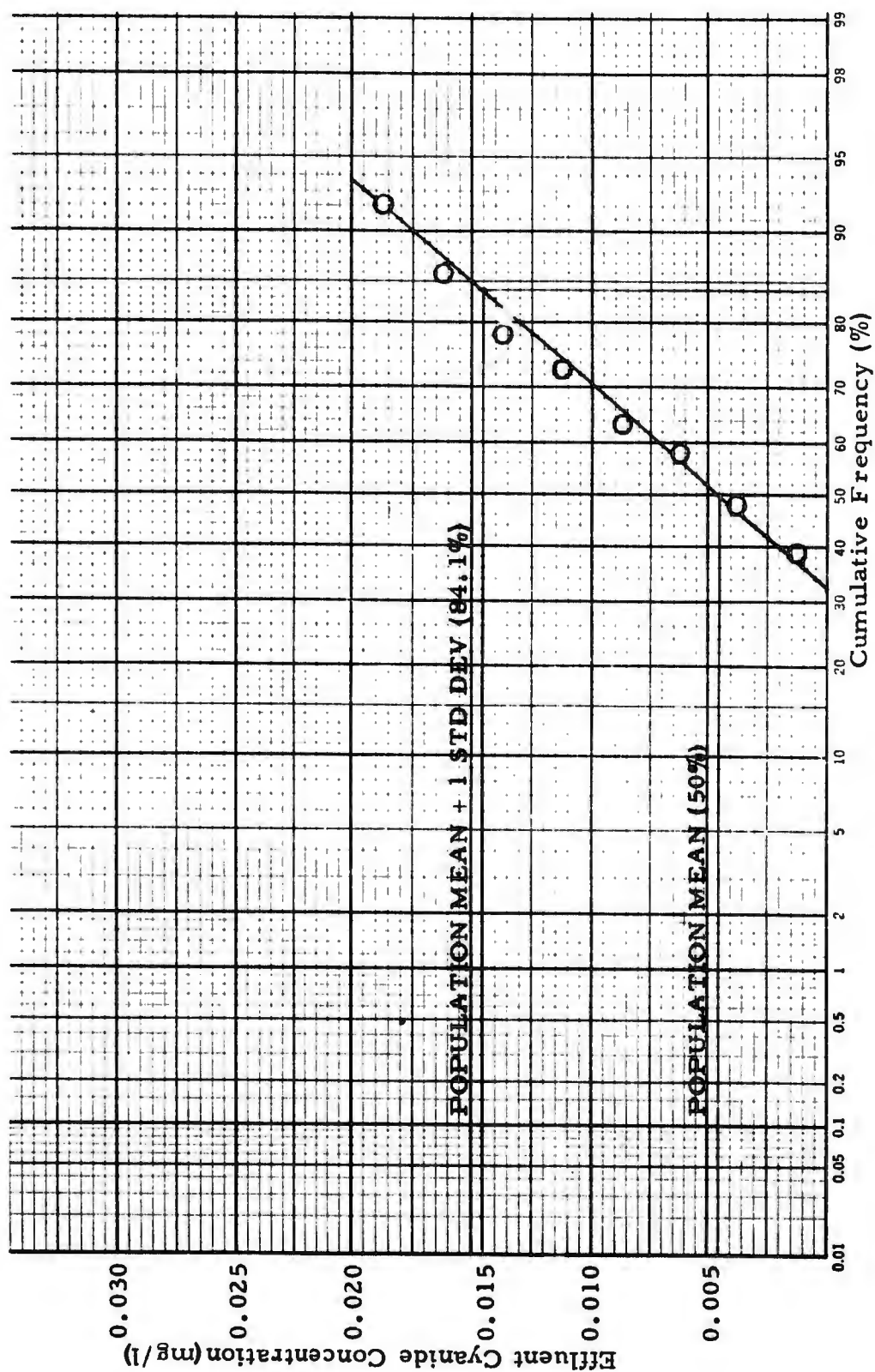


Figure 18. Fractile Diagram Effluent Cyanide Concentration

TABLE 19
ANALYSIS OF PROTOTYPE EFFLUENT

Sample Identification	TDS (%)	CO ₃ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	ClO ₃ ⁻ (mg/l)	Si (mg/l)	Fe (mg/l)	Al (mg/l)	Cu (mg/l)	Cd (mg/l)	Ag (mg/l)	Ni (mg/l)	Mn (mg/l)	Cr (mg/l)
HAFB-8/02/74	3.08	13.4	203.9	204	9.25	2.83	2.55	1.85	2.37	0.80	0.89	0.52	1.29
HAFB-8/05/74	3.02	38.8	192.8	117	3.92	0.94	1.15	0.69	1.69	0.30	0.60	0.66	0.91
HAFB-8/06/74	2.84	159.2	92.2	116	4.83	1.11	1.96	0.51	1.25	0.37	0.82	0.34	2.27
HAFB-8/07/74	2.93	108.2	121.8	79	15.81	3.51	19.31	2.05	2.05	0.53	1.08	1.17	1.00
HAFB-8/08/74	2.97	122.4	141.8	96	9.51	1.66	1.90	1.19	3.86	0.48	1.93	0.51	3.27
HAFB-8/09/74	2.72	107.2	151.9	85	10.08	5.45	3.54	2.59	2.45	0.49	2.12	1.17	2.70
HAFB-8/19/74	2.13	92.8	138.8	66	6.80	0.83	0.70	0.64	0.94	0.49	0.47	0.45	0.94
HAFB-8/22/74	0.08	95.0	165.1	9	3.21	1.49	0.07	0.57	3.68	0.32	0.06	0.08	0.78
HAFB-8/27/74	2.31	45.0	210.0	110	13.42	2.27	2.78	1.69	3.01	0.23	0.58	1.0	1.27

Essentially all of the TDS is NaCl which is purposely added to the liquid as a source of chloride for the generation of hypochlorite in the electrolytic cells. The system maintains the carbonate and bicarbonate concentrations sufficiently low to prevent scaling of the piping, probes, and flowmeters and to allow the cells to operate efficiently. The heavy metal concentrations are all very low. No explanation is offered for the obvious error in the TDS of the 22 August 1974 sample.

Photograph No. 7 shows the system as installed at Hill AFB during the field tests.

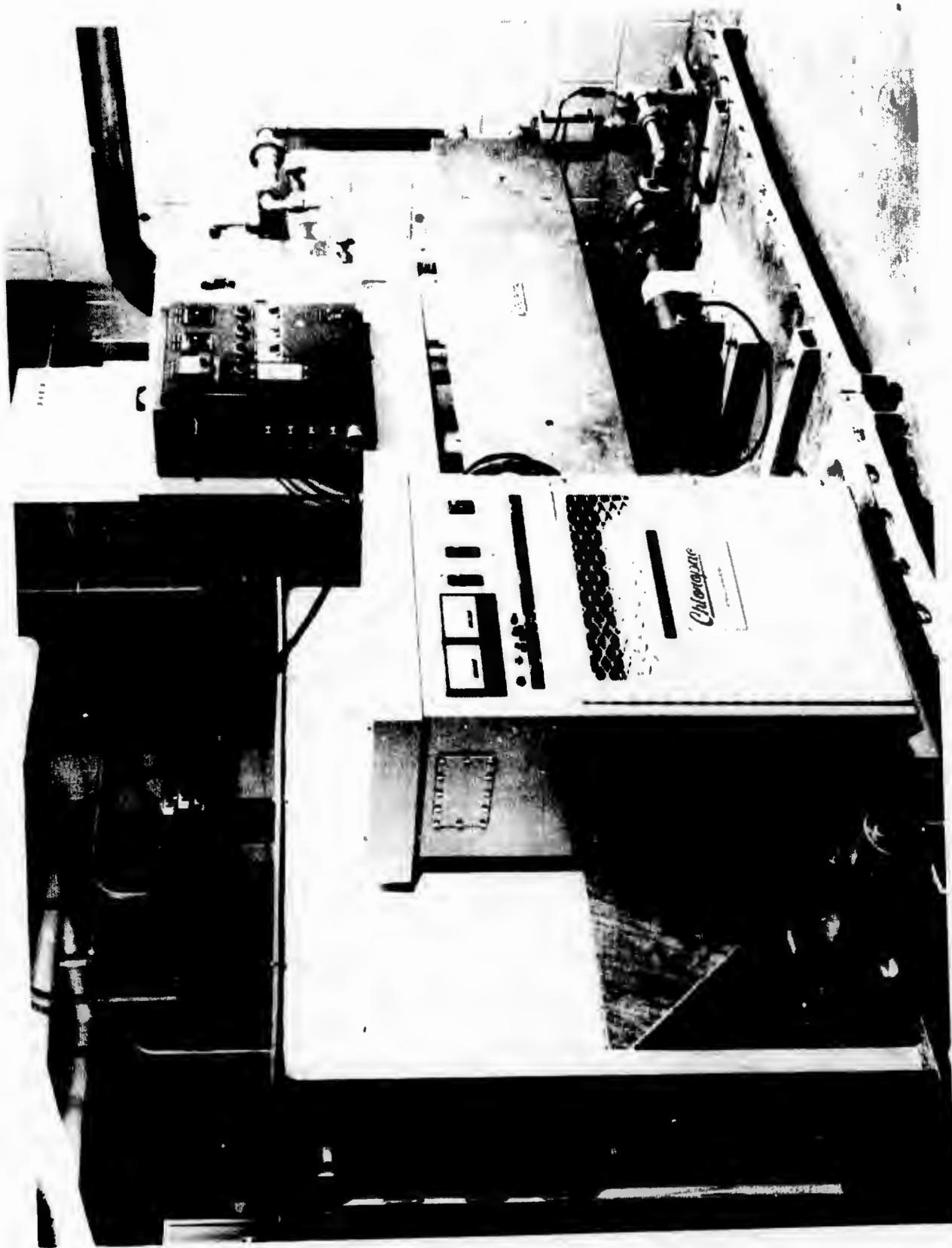


Photo No. 7. Thokol System As Installed at Hill AFB

SECTION V

PROTOTYPE SYSTEM EVALUATION

PERFORMANCE

The prototype cyanide destruct system was tested under field conditions with actual electroplating rinse water during a 30 day test period at Hill Air Force Base, as discussed in Section IV. In order to evaluate system performance during this test period, the effluent cyanide concentration data were arranged in Table 18 in concentration groups of 0.0025 mg/l increments. These data are presented graphically in Figures 17 and 18 to indicate the frequency distribution of cyanide concentrations in the effluent. It is observed that these data form a truncated population distribution with a mean value (50% cumulative frequency) of 0.0045 mg/l cyanide. The cyanide discharge standards for most states is in the range of 0.25 mg/l. Literature²⁶ indicates that future discharge standards may be as low as 0.025 mg/l. A comparison of these discharge standards with the above prototype performance data indicates that not only the population mean but also 100% of the effluent cyanide concentration values are well within existing discharge standards. The population mean and approximately 95% of the effluent cyanide concentrations are within the proposed future discharge standards.

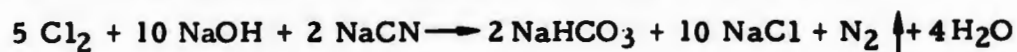
SAFETY

Alkaline chlorination of cyanide contaminated waste waters normally requires the shipping, handling, and storage of two hazardous chemicals: gaseous chlorine, and sodium hydroxide in both flake and solution forms. In addition, since most alkaline chlorinators operate at a pH of 11.0 to 11.5, hard water scale forms within the process equipment, requiring frequent cleaning using a concentrated acid, a third hazardous material.

The prototype cyanide destruct system generates the chlorine and sodium hydroxide in situ thereby eliminating personnel contact with these chemicals. Since the system operates at a pH of 8.0 to 8.5, hard water scale is not formed and the equipment does not require acid cleaning to remain operable. A small amount of hydrogen gas is generated by the prototype system as a by-product of chlorine and sodium hydroxide generation but is safely vented from the system as described in Section III.

OPERATING COSTS

The major portion of the operating costs for conventional alkaline chlorination is the cost of the two chemical additives, chlorine and sodium hydroxide. The theoretical chemical requirements for complete destruction of cyanides are derived from the following overall reaction:



$$\text{Cl}_2 \text{ Req} = 6.83 \text{ lb Cl}_2/\text{lb CN}^-$$

$$\text{NaOH Req} = 7.69 \text{ lb NaOH/lb CN}^-$$

These requirements will vary, of course, with the presence of additional contaminants such as cyanates, metal ions, ammonia, organics, etc, and with the pH of the waste water, but will be used as a basis of discussion. The raw material costs for conventional alkaline chlorination are shown below.

Chemical	Raw Material Costs (dollars/lb)		Raw Material Requirements (lb/lb CN)	Process Costs (lb CN)	
	Large Lot	Small Lot		Large Lot	Small Lot
	Purchase*	Purchase**		Purchase	Purchase
Chlorine	0.07-0.089	0.107-0.266	6.83	0.48-0.61	0.73-1.82
Sodium Hydroxide	0.125-0.135	0.215-0.257	7.69	0.96-1.04	1.65-1.98
				1.44-1.65	2.38-3.80

In the prototype cyanide destruct system, these chemicals are generated in situ by an electrolytic process. The economics of this process, based upon calibration data, is presented in Table 20. A graphical interpretation of these data is given in Figure 19, relating treatment costs per pound of cyanide with the cell current at salt concentrations of 1, 2 and 3%. The shaded areas represent the cost of conventional alkaline chlorination chemicals calculated based on small and large purchase lots.

These data indicate that the costs of power and salt are in opposition. High salt concentration promotes cell efficiency and reduces power costs. Salt consumption costs are high, however. Low salt concentrations retard cell efficiency and increase power costs. Salt consumption costs are reduced. However, it can be seen from the figure that electrolytic generation of chlorine and sodium hydroxide in situ is considerably less expensive than the relative purchase costs of the materials. Proper design and tailoring of a system to a given wastewater and optimization of power and salt consumption should provide a considerable savings potential in operating costs over conventional alkaline chlorination.

*Large lot purchase costs derived from Chemical Marketing Reporter,
11 Nov 1974; f.o.b. New York

Chlorine, tanks single units, works, freight equalized	7.00-8.90/100 lb
Soda, caustic, flake, 76%, 400 lb drums, car lot, works	12.50-13.50/100 lb

**Small lot purchase costs quoted by Wasatch

Chemical Co, Salt Lake City, Utah

Chlorine	39.90/150 lb cyl
.	214.00/1 ton cyl
Soda, caustic, flake	25.70/100 lb sack
Crystals	97.00/450 lb drum

TABLE 20
OPERATING COST SUMMARY
THIOKOL PROTOTYPE CYANIDE DESTRUCT SYSTEM
(Process Rate = 0.5 gal/min)

Salt		Electr Cell			Cl ₂ Generation		Requirements		Theoretical Operating Costs			
Conc (%)	Usage (lb/day)	Current (amps)	Potential (volts)	Power (kw-hr/day)	Conc (mg/l)	Output (lb Cl ₂ /day)	$\left(\frac{\text{kw hr}}{\text{lb Cl}_2}\right)$	$\left(\frac{\text{lb salt}}{\text{lb Cl}_2}\right)$	Power* $\left(\frac{\text{dollars}}{\text{lb Cl}_2}\right)$	Salt** $\left(\frac{\text{dollars}}{\text{lb Cl}_2}\right)$	Total $\left(\frac{\text{dollars}}{\text{lb CN}}\right)$	Total***
1	59.8	100	11.4	27.4	1,100	6.57	4.17	9.10	0.0417	0.076	0.118	0.81
1	59.8	200	14.8	71.0	2,200	13.15	5.40	4.55	0.0540	0.038	0.092	0.63
2	119.5	100	9.5	22.8	1,700	10.10	2.24	11.76	0.0224	0.098	0.120	0.82
2	119.5	200	11.2	53.8	3,000	17.93	3.00	6.66	0.0300	0.055	0.085	0.58
2	119.5	300	12.4	89.3	3,800	22.71	3.93	5.26	0.0393	0.044	0.083	0.57
2	119.5	400	13.3	127.7	4,600	27.49	4.65	4.35	0.0465	0.036	0.083	0.57
3	179.3	100	9.0	21.6	1,800	10.76	2.01	16.66	0.0201	0.138	0.158	1.08
3	179.3	200	10.5	50.4	3,150	18.82	2.68	9.53	0.0268	0.079	0.106	0.72
3	179.3	300	11.4	82.1	4,600	27.49	2.99	6.52	0.0299	0.054	0.084	0.57
3	179.3	400	11.3	108.5	5,800	34.66	3.13	5.17	0.0313	0.043	0.074	0.51

*\$0.01 kw-hr.

**Costs quoted by Lake Crystal Salt Co., Salt Lake City, Utah,
water softener grade, fine, 100 lb sack, \$16.60/ton.

***6.83 lb Cl₂/lb CN.

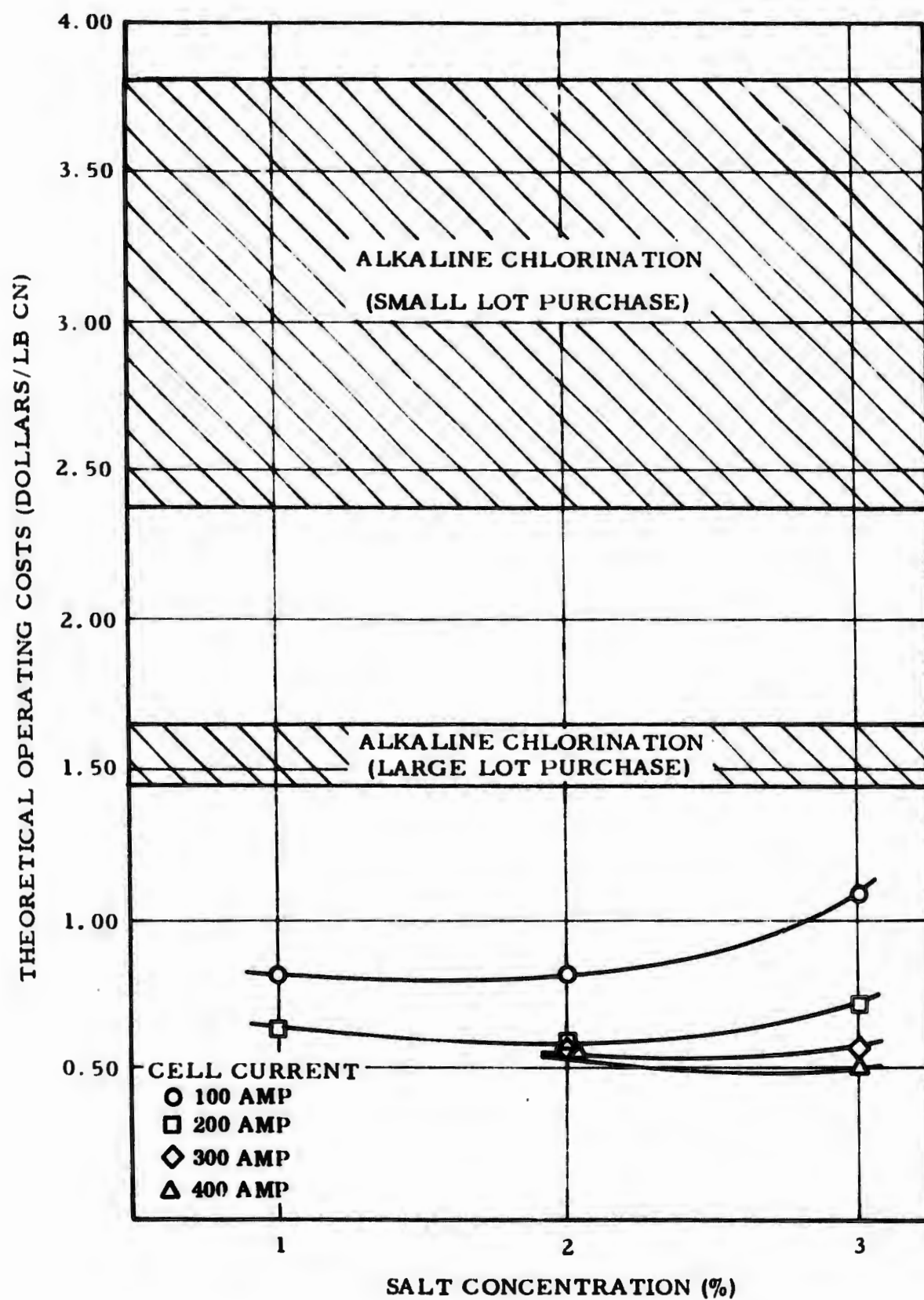


Figure 19. Operating Cost Summary

SECTION VI

INTEGRATED SYSTEM

A cyanide destruct system which returns the treated wastewater back to the plating operation for reuse as shown schematically in Figure 20 represents a process step which has been integrated into the overall plating operation. Such a cyanide system is called an integrated system.

A subscale integrated cyanide waste treatment system was set up for testing and evaluation. A flow schematic for the system is shown in Figure 21. The total liquid volume of the system was approximately 82 liters. A 50 in² PEPCON electrolytic cell was used to generate the hypochlorite for cyanide destruction. The system was designed to simulate a full-scale unit operating in an actual plating facility.

The rinse tank represents a rinse tank in a plating line. Cyanide carryover by plated parts from the plating tank is simulated by the addition of concentrated plating waste to the rinse tank. The overflow from the rinse tank passes to the recycle tank where it is pumped through the electrolytic cell at a flow rate of approximately 10 times the rinse tank overflow rate. Hypochlorous acid and sodium hypochlorite are generated within the cell via chemical and electrochemical reactions. Acid is added to the liquid at this point for pH, carbonate, and bicarbonate control. The treated liquid overflows to the settling tank for solids removal and is then pumped back to the rinse tank for reuse.

The system was initially charged with a 3% NaCl solution with 0.05% MgCl₂ added to prevent calcium scale buildup on the cathode of the cell. The cell was operated to maintain approximately 50-100 mg/l total residual chlorine in the final settling tank.

During the operation of the system it was necessary to add sufficient volume of liquid to allow the extraction of samples for analysis and also to condense the "real" operating time of the system to fit program schedules. Both of these requirements were satisfied by adding larger volumes of

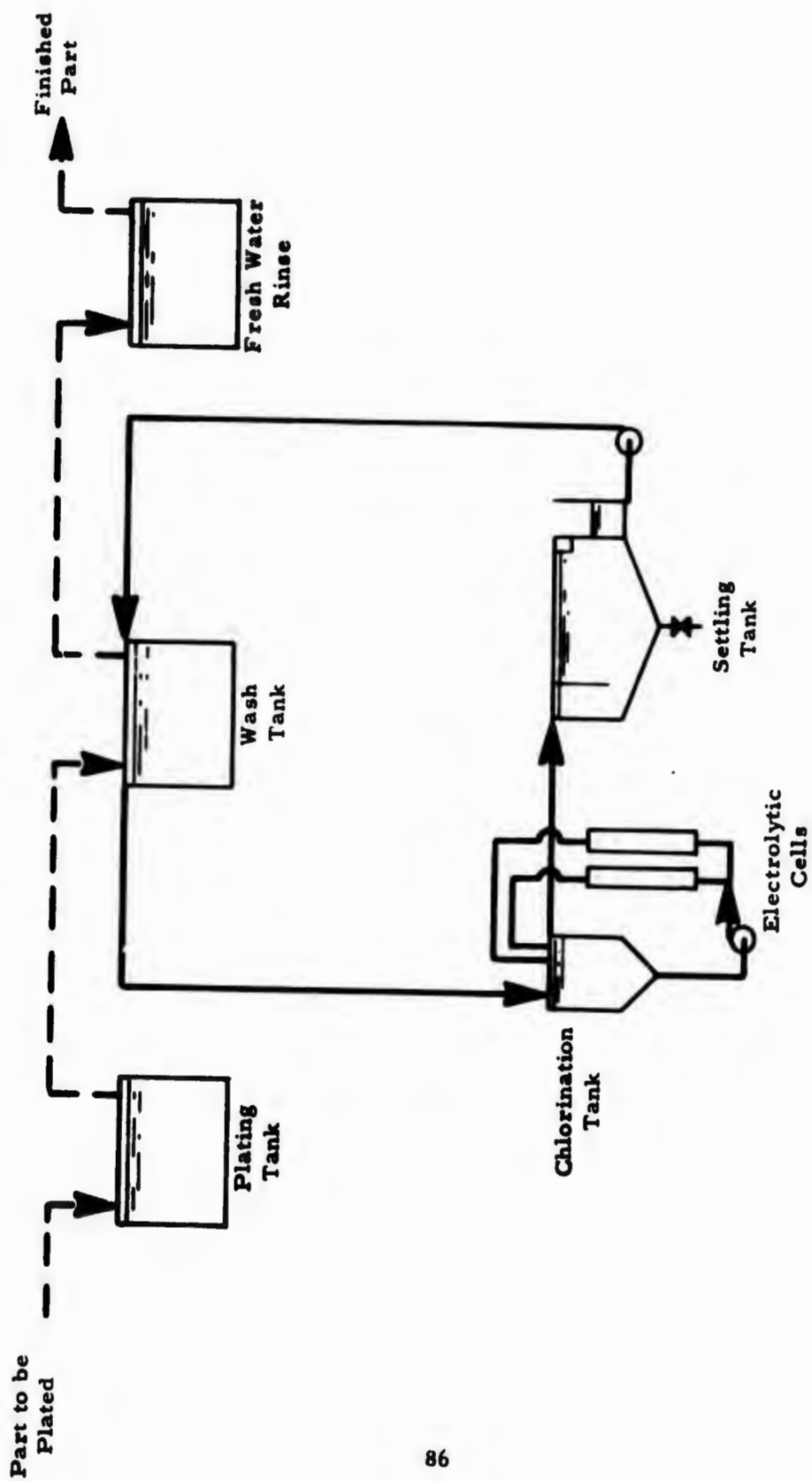


Figure 20. Integrated Cyanide Destruct Process With Total Recycle Using Thiokol Treatment System

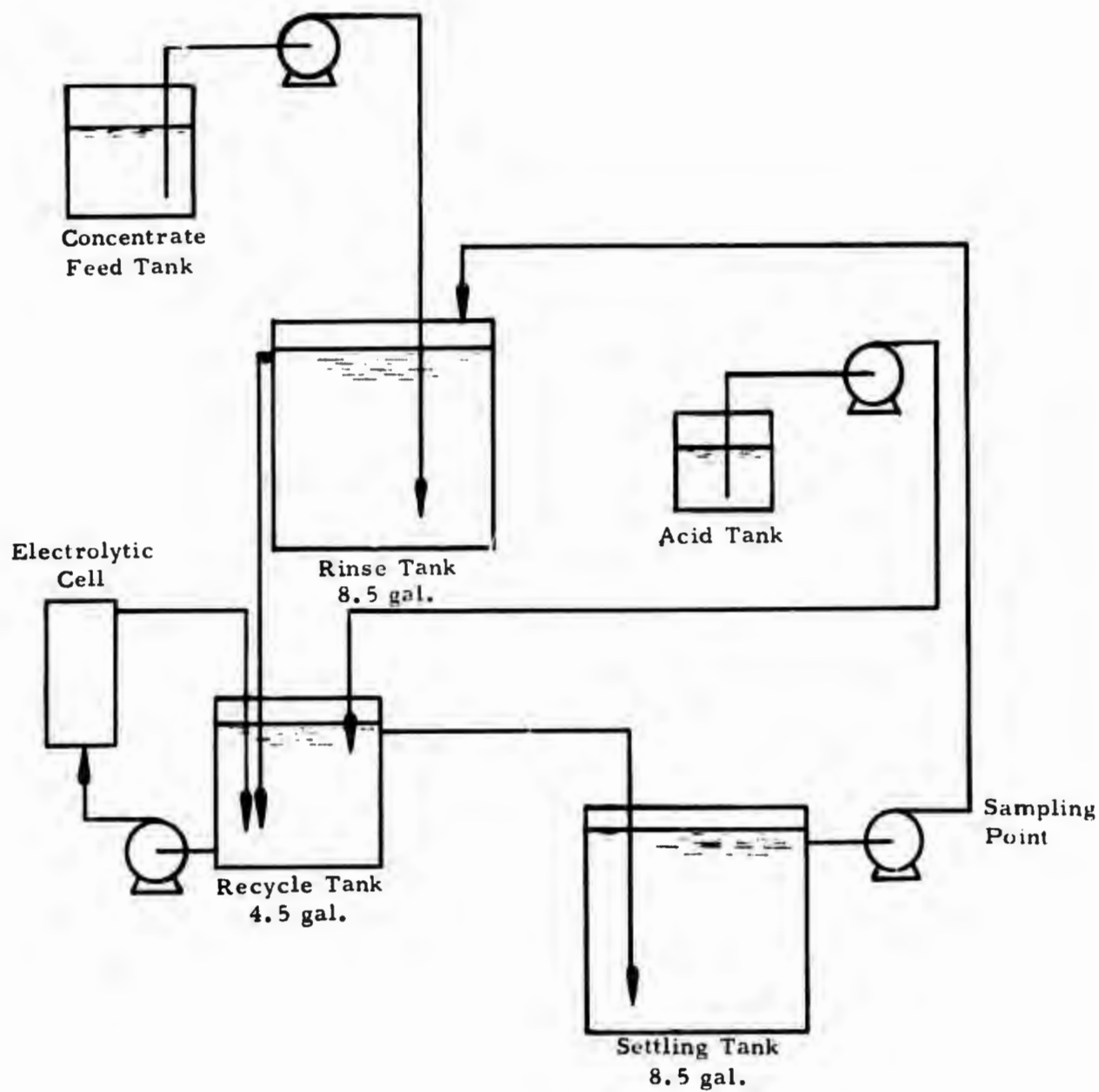


Figure 21. Integrated (Recycle) Cyanide Waste Treatment System, Subscale

concentrated cyanide waste liquids than one would see as liquid carryover in an actual system. Since no data were available which would allow an exact number to be placed on the amount of plated-part liquid carryover, the degree of time-scale condensation could only be estimated.

Concentrated solution was added to the system at a rate of approximately 1 ml/min or 480 ml/8-hr day. A direct scaleup from the 82 liter system to a 1,000 gallon system predicts a part carryover of approximately 6 gallons per 8-hour day. This is estimated to be about a factor of 10 excessive; therefore, each day of operation of the subscale system would be equivalent to 10 days for the 1,000 gallon system with regard to the amount of cyanide, Metex, and other materials having a chlorine demand fed to the system. Of equal importance is the effect of this factor on residence time of chlorine-consuming compounds in the liquid.

A summary of all the test data is presented in Table 21. The system was operated for 20 calendar days or approximately 31 eight-hour days and samples were taken at periodic intervals. The samples were withdrawn from the treated recycle liquid line as shown in Figure 21. Figure 22 shows the cyanide and cyanate levels during the operating periods. The cyanide and cyanate were much lower when the pH was controlled and kept between 7 to 7.5. The cyanide level was generally less than 5 mg/l and by raising the chlorine level it could be reduced to 2 mg/l or below. The carbonate and bicarbonate can be maintained at a reasonable level by the addition of acid and by maintaining a high chlorine level. This can be seen in Figure 23. There is a gradual increase in chlorate but this stabilized during the 8 to 16 day operating period and then increased during the last few operating days (see Figure 24). The chloride dropped after the fifth day due to the loss of liquid from the settling tank. After the ninth day the liquid was lost from the rinse tank but salt water was added to bring it up to volume. There is a gradual increase of chloride due to hydrochloric acid addition but this leveled off at 26,000 mg/l chloride. This chloride level is equivalent to a 4% salt solution, and is only a 1% increase of salinity over the total operating period of the system.

TABLE 21
DATA SUMMARY FOR THE LABORATORY INTEGRATED SYSTEM TESTING

Sample Identification*	Concentration (mg/l)						pH	Remarks
	CN ⁻	CNO ⁻	ClO ₃ ⁻	CO ₃ ⁻	HCO ₃ ⁻	Cl ⁻		
IS-6/19/74-2300-Cd	8.5	39.9	730	381	1,098	19,854	90	7.8
-6/20/74-1600-Cd	-	-	957	400	1,424	20,025	100	7.9
-2300-Cd	0.72	10.5	1,530	772	1,572	20,196	580	8.0
-6/21/74-1600-Cd	-	-	1,936	483	2,897	18,998	110	8.0
-2300-Cd	10.0	77.7	2,400	944	3,850	19,460	90	8.4
-6/24/74-1700-Cd	-	-	2,490	633	3,439	15,404	140	8.6
-2300-Cd	5.0	29.4	3,642	880	3,884	15,746	50	8.7
-6/25/74-1500-Cd	-	-	4,058	523	4,054	16,516	140	7.5
-2300-Cd	16.3	117.6	4,935	1,124	4,433	16,430	110	8.7
-6/26/74-2300-Cd	2.5	10.5	-	-	-	-	500	7.0
-6/27/74-1500-Cu	41.2	178.6	-	-	-	20,658	110	8.2
-2300-Cu	-	-	3,806	0	4,813	21,101	70	7.7
-6/28/74-2100-Cu	-	-	3,886	544	2,371	22,336	900	7.2
-6/28/74-2100-Cu	1.25	319.5	-	-	-	-	720	7.1
-7/01/74-1100-Cu	2.5	233.2	-	-	-	-	-	-
-7/02/74-1500-Cu	0.15	8.4	4,757	120	717	24,475	60	7.2
-2300-Cu	0.18	16.8	5,170	56	1,408	25,450	40	7.5
-7/03/74-2300-Cu	10.0	12.6	3,615	178	1,894	26,391	540	8.0
-7/09/74-0815-Ni	0.065	2.1	5,301	0	-	25,530	110	5.8
-2300-Ni	1.7	23.1	5,459	187	344	26,676	90	7.3
-7/10/74-2300-Ni	0.71	36.6	5,291	228	882	24,988	110	7.3
-7/11/74-0700-Ni	0.28	0.84	-	-	-	-	100	6.6
-2300-Ni	0.41	9.2	5,531	240	960	25,500	110	7.1
-7/12/74-2300-Ni	5.0	117.6	6,062	End-Point Masked	26,370	100	100	7.5
-7/16/74-2300-Ni	4.3	16.8	6,305	219	1,682	25,672	520	5.0
-7/17/74-2300-Ni	3.8	16.8	6,464	46	1,981	25,560	140	7.4
-7/19/74-0730-Ni	2.0	2.1	7,345	0	630	26,345	640	7.4

*IS - (Date sample was taken) - (Time sample was taken) - (Cation of waste)

Figure 22. Integrated System Cyanide/Cyanate Content

Figure 23. Integrated System Carbonate/Bicarbonate Content

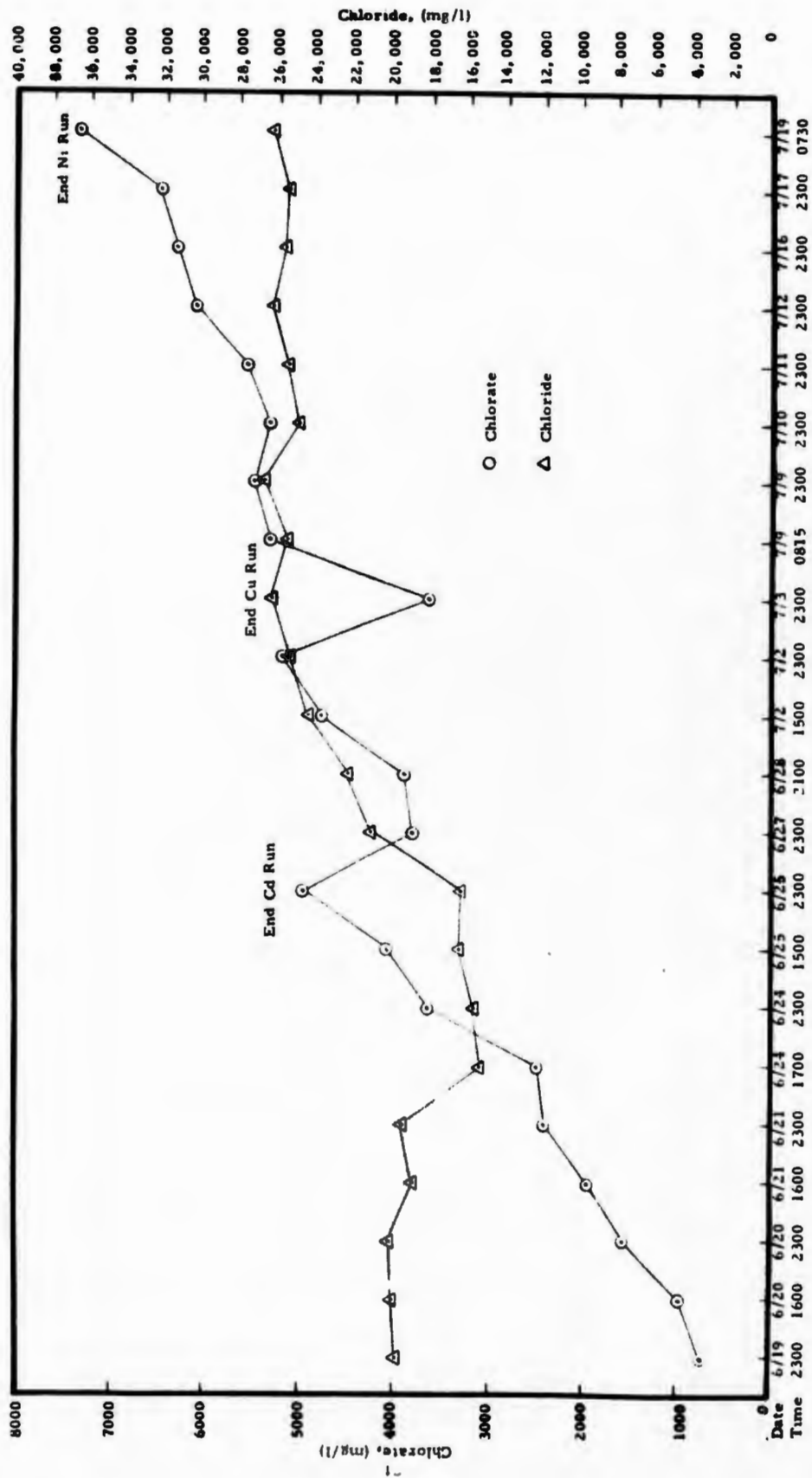


Figure 24. Integrated System Chlorate/Chloride Content

The amount of cyanide waste added was 14.7 liters or 18% of the total volume of the system. This would be equal to 180 gallons in a 1,000 gallon system. Assuming the above estimate of 0.6 gallons per day dragover from the plating tanks, this would represent 300 real-time 8-hour days or 1.15 years of operation (8 hr/day, 5 days/week). The recycle liquid after this period of time had stabilized with regard to cyanide, cyanate, chloride, carbonate, and bicarbonate content. The chlorate continued to increase but was less than 1% at the end of the test. The cyanide and organic materials found in the cadmium strip, copper plating waste, and nickel strip were removed by the integrated system. It was determined during the cadmium testing that acid must be added to maintain the pH around 7. This is necessary to keep the bicarbonate level low enough to maintain the proper chlorine generation rate of the electrolytic cells.

The system was started using a cadmium strip concentrate as feed liquid. A break in the system tubing at 2100 on 21 June caused the liquid in the settling tank to be drained. Raw water only was added to refill the tank and the test was continued. On 25 June at the end of the cadmium strip run the rinse tank was inadvertently drained overnight. Salt water was added to bring the system up to the proper level for operation. The system was then run for approximately 8 hours to raise the chlorine level to about 500 mg/l and the pH was adjusted to 7.0 with hydrochloric acid. By so doing, the yellow "Metex" color was removed and the liquid became very clear. The small amount of precipitate that was formed was removed using a cartridge filter. The cyanide concentration of the cadmium strip feed for this test was 62,000 mg/l. A total volume of 4.5 liters of cadmium strip concentrate was added to the system during this test.

The next feed liquid tested was a copper plating waste with a cyanide level of 80,000 mg/l. The total amount of concentrate added during the test was 4.1 liters. The copper cyanide solution was added to the system liquid

which remained after the final cadmium treatment runs, i.e., the system was not purged prior to the addition of copper waste.

A large quantity of copper oxide was formed during the treatment process and was satisfactorily removed by settling and filtering at the end of the final treatment. The copper cyanide feed was started on 27 June at 0800. At 1500 the acid pump was turned on and used continuously for all subsequent treatment. Prior to this the pH was adjusted in a batchwise manner. On 28 June at 1430 the cyanide feed pump failed to operate because of an air lock. Consequently, the injection of fresh concentrate ceased which allowed the chlorine level to rise. This also produced a low cyanide level in the effluent. The copper test was discontinued on 3 July. The chlorine level was increased to 580 mg/l. The pH level was also increased to a level of 8.0. The copper oxide precipitate was removed on 8 July and the system was run for the rest of the day to build up a high chlorine level to remove the organic materials from the liquid and to obtain a low cyanide level. The liquid was clear in appearance and had a light green color. The 0815 data point on 9 July was for the sample taken from the system after the final treatment of the copper cyanide. The cyanide and cyanate levels were very low.

Nickel strip with a cyanide concentration of 35,000 mg/l was then fed into the system until a total of 6.1 liters was added. The liquid in the system became very dark by 12 July because of the color imparted to it by the Metex. This made it difficult to measure the chlorine level. The system was operated on 16 July with the feed pump off. This was done to allow the hypochlorite to clear up the dark color of the liquid. The system was then operated with a nickel cyanide feed for 8 hours on 17 July and 1/2 day on 18 July. The system was run all night on 18 July and a sample taken at 0730 on 19 July. The cyanide and cyanate level were about 2 mg/l and the recycle liquid had a very light greenish yellow color and was clear.

The tests on the laboratory integrated recycle system have shown that such a system can treat large quantities of concentrated cyanide wastes over an extended period of time. The recycle liquid after the equivalent period of 1.15 years was still clear with only a slight color. The full life of the system could be equal to several years before the liquid would have to be discarded. The recycle liquid maintained a low cyanide level. In an actual operation, one would undoubtedly use a fresh water rinse after the rinse of a plated part in the recycle liquid. Because the cyanide level is maintained at such a low level in the recycle liquid, any cyanide carryover by the plated part to the fresh water rinse tank would be so low as to make the cyanide level in the fresh rinse water too low to measure.

In the laboratory system the concentrate feed was stopped to allow the system to build a chlorine concentration sufficiently high and/or to allow enough residence time to destroy the organic materials in the liquid. In a full scale system this would probably not be required. The system would be designed to provide sufficient residence time and the pH would be continuously controlled in the 6-7 range to ensure the presence of the most reactive hypochlorite species, HOCl. On a real time equivalent basis and based on the time-scale assumptions cited earlier, the lab system treated in one day the amount of cyanide a full scale system would see in about a month. This added residence time would have a beneficial effect on the recycle liquid by allowing time for the very slow chlorine-organic material reactions to occur.

The integrated system had a cyanide level comparable to that in the prototype flow-through system even after 20 calendar days of operation. The iron cyanides which are found in the treated cyanide waste must gradually decompose in the integrated system since the total cyanide level stays almost the same as treatment time progresses.

The design of a full scale integrated system would probably include a chlorine controller to operate the electrolytic cell to maintain a constant

hypochlorite level in the recycle liquid. The pH in the recycle tank would be controlled by the addition of hydrochloric acid. In the laboratory system 2-1/2 liters of concentrated acid were added during the test period. This is equivalent to about 30.5 gallons in 1.15 years in a 1,000 gallon system or 2.2 gallons per month using the scaleup assumption discussed above.

The addition of salt should not be required. To prevent calcium deposits on the electrolytic cell and tanks, a small amount of magnesium chloride would be added periodically.

The integrated system has many advantages over a flow-through system. All the chlorine is used to treat cyanide and none is discharged. Large quantities of water would be saved which are now used for rinse water. No cyanide is discharged except for that in the dragout from the fresh water rinse which would be undetectable. The cyanide on the plated part is treated immediately by chlorine in the rinse tank so there is no concentrated cyanide waste on the part or in the rinse bath.

SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

A cyanide destruct system has been developed and field tested which will effectively remove cyanides from the wastewater of an electroplating facility. The field testing was carried out with the system taking wastewater directly from the overflow tank of a cyanide plating rinse line. The maximum concentration of cyanide in the influent wastewater was 47 mg/l. The maximum cyanide concentration in the destruct system effluent was 0.05 mg/l and less than 0.02 mg/l for 94 percent of the samples taken during operation. The population mean for the cyanide concentration of all samples was 0.0045 mg/l. A comparison of these numbers with the 0.25 mg/l range which is the standard for most states establishes the adequacy of the system for handling wastes of the type tested.

Laboratory testing prior to the field tests showed that the treatment system could effectively handle cyanide concentrations up to 10 times greater than those found during the field tests.

Techniques and methods for analyzing aqueous cyanide plating solutions were developed for measuring cyanide accurately down to 0.002 mg/l. The analytical procedures developed during this program require the use of the tartaric acid distillation method rather than the sulfuric acid method because of the problem of chlorate decomposition at the low pH levels used in the sulfuric acid distillation. Residual cyanide that might be present in the sample prior to analysis is destroyed when the chlorate is decomposed.

For the standard colorimetric analysis, it was discovered that the pH must be controlled much more precisely than is recommended in the standard procedure. It was found that, for cyanide concentrations less than about 1 mg/l, a pH of 6.1 ± 0.05 produced the best precision and accuracy, although a slightly higher pH could be used if it is maintained at a constant level. In addition to pH control, residual chlorine neutralization using sodium sulfite

must be accomplished with precision. An excess of sodium sulfite over that required for residual chlorine neutralization was found to interfere with the color development reactions in the analysis.

The Thiokol system design has eliminated the problems associated with transporting, storing, and feeding the chlorine gas and caustic as well as the problems of probe fouling and carbonate scale buildup found in standard alkaline chlorination systems. No scale buildup was observed in the system during the program.

It is recommended that pH, chlorine, and cyanide electrodes be installed at proper points in the system and that these probes be wired to strip chart recorders to provide a continuous record of the performance of the system.

The laboratory study of the integrated system approach to cyanide treatment showed the basic Thiokol design to have great promise in this application. It is recommended that an R&D program be initiated to design, fabricate, and test a full scale integrated system and that the system be finally installed as an integrated process in an actual electroplating facility.

The prototype unit as field tested at Hill AFB, Utah, had a hydraulic capacity of only 0.5 gpm. For the rinse wastes that were processed by the unit at Hill AFB, the equivalent cyanide destruct capacity is approximately a factor of 10 greater. It is, therefore, recommended that the minor modifications required to convert the system to handle 5 gpm be made and that the unit then be tested extensively to determine actual capacity and performance over an extended period of time.

The basic cyanide treatment system prototype developed during this program had no provision for automatically monitoring, recording, or controlling pH, chlorine, or cyanide. For a further test program to be useful, the performance of the system should be measured by analyzing the discharge stream for pH,

residual chlorine, and any residual cyanide and the incoming wastewater should be analyzed for its cyanide concentration.

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APPENDIX A

LABORATORY TESTS

Carbonate and Bicarbonate

A 1/50th-scale laboratory system was set up with a flow-through mode of operation. The system was operated at 20 amps and 60°F with a 3% salt solution. The bicarbonate level was artificially brought to 6%. The result was a 60% drop in the chlorine generation rate. With a PEPCON cell the reduction was approximately 10 to 1 under the same conditions (see Table A-1). Another test was run under the same conditions but with the temperature and bicarbonate levels one might expect in the prototype system, i. e., 100°F and 1,500 mg/l bicarbonate. The same current density was used in both the PEPCON and the Engelhard cells. There was a small decrease in chlorine generation with the PEPCON cell. No bicarbonate effects were observed with the Engelhard (see Table A-2). The laboratory cell was fabricated by Engelhard using a platinized titanium wire mesh screen anode rather than their standard design of platinized titanium tubing. Hence, only the relative effects of temperature and bicarbonate should be considered here and not the chlorine production rate of the two cells. The production rate and treatment capacity of the full scale cells must obviously be ascertained in a full scale test.

Activated Carbon

A solution of nickel plating waste material containing approximately 600 mg/l cyanide and 2% NaCl was prepared. The solution was circulated through the PEPCON cells for three hours with fresh nickel solution being added to the circulating material at a rate of 10 to 25 ml per minute. At three hours the material was transferred to a holding tank at a rate of 25 ml per minute. After two additional hours in the holding tank, the material was

TABLE A-1
EFFECT OF 6% BICARBONATE ON ELECTROLYTIC CELLS

	<u>3% Salt Chlorine Concentration (mg/l)</u>	<u>3% Salt/6% Bicarbonate Chlorine Concentration (mg/l)</u>
Engelhard Cell	823	385
PEPCON Cell ¹¹	950	85

TABLE A-2
EFFECT OF 1,500 MG/L BICARBONATE AND
100°F ON ELECTROLYTIC CELLS

	<u>3% Salt Chlorine Generation (mg/l)</u>	<u>3% Salt/1500mg/l Bicarbonate Chlorine Generation (mg/l)</u>
Engelhard Cell	818	836
PEPCON Cell	1,053	970

pumped through a 1.5 in. diameter column containing 300 grams of activated charcoal. Two types of charcoal, Barnebey-Cheney type PC and Filtrasorb-400 were evaluated. Exposure time to each charcoal was approximately 30 minutes. Samples were taken at three hours circulation through the PEPCON cells, after one hour and after two hours in the holding tank, and after exposure to each of the activated charcoals. Analyses were made by tartaric acid distillation and titration of the untreated sample and colorimetric analyses of the treated samples. Data are shown in Table A-3.

The PC charcoal appears more selective than the Filtrasorb charcoal. However, neither type produced a significant improvement in effluent quality.

In order to ensure that an excess of hypochlorite was generated by the PEPCON cells, the hypochlorite level was monitored at 30 minute intervals. Data are presented in Table A-4. It was apparent that a feed rate of 25 ml per minute was too high for 2% NaCl for 20 amp current with the nickel waste. The OCl^- level reached a low of 5.5 mg/l. The flow was reduced to 10 ml per minute. This reduction resulted in a gradual increase in excess hypochlorite. At 255 mg/l the OCl^- was reaching a higher excess than desired; hence, the flow rate was increased to 15 ml per minute. The OCl^- concentration dropped and then continued to decline gradually. It was concluded, therefore, that the optimum flow rate for this system would be approximately 12 to 13 ml/min.

It should be noted that previous work with nickel waste using 3% NaCl provided ample hypochlorite with the same power. Two percent NaCl is sufficient for copper plating wastes at approximately the same cyanide concentration. Since the chlorine generation rate of the cells is directly related to the chloride concentration of the electrolyte, the data indicate that more chlorine is required to treat the nickel waste than the copper waste at the same cyanide concentration. This additional chlorine demand arises from the organic material (Metex) in the nickel waste. Also, for oxidation

TABLE A-3
Nickel Plating Waste at 2% NaCl Treated
with Activated Charcoal

<u>Sample Treatment</u>	<u>CN⁻ Concentration (mg/l)</u>	
	<u>Titration</u>	<u>Colorimetric</u>
Influent (untreated)	675.0	-
PEPCON (3 hr)	-	0.132
PEPCON (3 hr) + Holding Tank (1 hr)	-	0.081
PEPCON (3 hr) + Holding Tank (2 hr)	-	0.075
PEPCON (3 hr) + Holding Tank (2 hr) + Type PC Charcoal	-	0.013
PEPCON (3 hr) + Holding Tank (2 hr) + Filtrisorb Charcoal	-	0.068

TABLE A-4
Nickel Plating Waste at 2% NaCl
Hypochlorite Monitoring

<u>PEPCON Treatment Time</u>	<u>Hypochlorite (mg/l)</u>	<u>Feed Rate of Untreated Material (ml/min)</u>
30 min	25.0	25
1 hr	5.5	25
1.5 hr	16.6	10
2.0 hr	15.0	10
2.5 hr	40.0	10
3.0 hr	74.0	10
3.5 hr	80.0	10
4.0 hr	255.0	10
4.5 hr	50.0	15
5.0 hr	35.0	15
5.5 hr	30.0	15
6.0 hr	20.0	15

of the metal ions, 2.25 parts of chlorine are required per part of nickelous nickel whereas only 0.56 parts of chlorine are required per part of cuprous copper.

UV Irradiation

A laboratory scale system was assembled to test the PEPCON cells in conjunction with an ultraviolet light radiation cell. Samples were processed to check out the system and evaluate treatment effectiveness.

A solution of potassium cyanide of approximately 2,000 mg/l with 3% NaCl was first prepared and circulated through the PEPCON cells only, operated at 10 amps each, for a period sufficient to generate an excess of hypochlorite. The cyanide concentration was measured at 5.0 mg/l by titration with silver nitrate.

The solution was then circulated through both the PEPCON cells and the ultraviolet radiation cell for an additional one-half hour. The product was analyzed by the colorimetric method after distillation. The results are shown in Table A-5.

A 40:1 dilution of nickel plating waste was prepared with 3% salt added. Untreated material was fed into the reaction tank at a rate of 25 ml/min.

The material was treated by the PEPCON cells alone for 2.0 hours to generate an excess of hypochlorite, then circulated through the ultraviolet irradiation cell for 0.5 hours. A sample was taken for analysis at the 2-hour point and then at the 2.5-hour point. The material had thus been circulated through the PEPCON cells for a total of 2.5 hours and the ultraviolet cell for 0.5 hours. One sample was taken before the material entered the UV cell and another sample was taken after the material had been through the UV

TABLE A-5
DECOMPOSITION OF 2000 mg/l KCN

Sample Description	CN ⁻ Concentration (mg/l)	
	Tartaric Acid Distillation Titration	Sulfuric Acid Distillation Titration
KCN with 3% NaCl - untreated	1860	1820
PEPCON Cell Only - 1 hr	622	618
PEPCON Cell Only - 3 hr	5.0	5.0
PEPCON Cell - 3-1/2 hr UV - 1/2 hr	0.16	0.14

TABLE A-6
DECOMPOSITION OF NICKEL WASTE (40:1 dilution)

Sample Description	CN ⁻ Concentration (mg/l)	
	Tartaric Acid Distillation Titration	Sulfuric Acid Distillation Titration
Ni Waste - Untreated	770	700
Treated - 2 hr PEP CON Only	5.0	5.0
PEPCON - 2-1/2 hr before UV	0.43	0.36
PEPCON - 2-1/2 hr after UV	0.42	0.38
PEPCON + UV - 5 hrs before UV	14.0	10.0
PEPCON + UV - 5 hrs after UV	0.43	0.20

cell to give an indication of the effect UV irradiation had on the material. A test was made using the UV light in the recycle loop with the PEPCON cell. Samples were taken after 5 hours of operation. A final pass was made through the UV light and cyanide was measured before and after passage through the light. A drop in cyanide was observed. Data are shown in Table A-6. The data from the experiments appear to disagree. The UV treatment appears to have a beneficial effect on the KCN solution and on the nickel waste at the 14 mg/l test but to have no effect on the nickel waste where the concentration was less than 1.

UV Irradiation Plus Activated Carbon

Samples of copper plating waste material containing approximately 500 mg/l cyanide were circulated through the PEPCON cells at a rate of one liter per minute for three hours, then transferred to a holding tank for a total of 5 hours, then pumped through an ultraviolet reaction chamber at a rate of 25 ml per minute. After this treatment the effluent was gravity filtered through activated charcoal columns of 6-14 mesh and 50-200 mesh particle sizes.

Samples for cyanide analysis were taken from the treatment system as follows:

- (1) Before treatment
- (2) After 3 hours of treatment using PEPCON cells only.
- (3) After 4 hours of treatment using PEPCON cells only.
- (4) After 4 hours reaction time in the holding tank.
- (5) After 4 hours reaction time in the holding tank followed by one pass through the UV cell.
- (6) After 5 hours reaction time in the holding tank.
- (7) After 5 hours reaction time in the holding tank followed by one pass through the UV cell.
- (8) Solution with the history of No. 7 passed once through a 6-14 mesh charcoal column.

- (9) Solution with the history of No. 7 passed once through a 50-200 mesh charcoal column.

The data from the analysis of these samples are shown in Table A-7. Analytical problems with the sulfuric acid method are apparent. There is significant scatter in the data although the downward trend of cyanide concentration indicates a beneficial effect of UV plus carbon.

The minimum level of cyanide detectability for these analyses was 0.01 mg/l. Lower limits of detectability could be achieved only by using larger sample volumes. The total volume of the laboratory system was too small to allow larger sample sizes.

In a second experiment, a quantity of copper plating waste at approximately 500 mg/l cyanide with 3% NaCl added was circulated through the PEPCON cells operated at a current of 20 amps and at a flow rate of 1 liter per minute for a total of three hours. When the hypochlorite reached a level of more than 150 mg/l, additional copper waste material was added to the stream at a rate of 25 ml per minute. The material was pumped into a holding tank after PEPCON treatment. The maximum treatment time before UV exposure was 4 hours. The solution was then passed once through the UV reactor and from there pumped at a rate of 25 ml per minute through 6-14 mesh activated charcoal. After a quantity had been treated as described above the UV reactor was turned off and the material was pumped through the activated charcoal without UV irradiation. Samples were taken and data are shown in Table A-8.

Because of problems uncovered in the standard analytical methods for colorimetric analysis the data shown in Tables A-7 and A-8 are of limited utility. However, the electrode data are sufficiently precise to see the general trend of the treatment stages. The electrode sees only free cyanide. Free cyanide appears to have been stabilized at about 0.004 mg/l. After UV irradiation more free cyanide was detected. These data indicate that possibly UV irradiation breaks down combined (complexed) cyanides or other chemical species in the cyanide family. The charcoal tested appears to be ineffective.

TABLE A-7
LABORATORY DATA

	CN ⁻ Concentration (mg/l)					
	Titration		Colorimetric		Electrode	
	Tartaric	Sulfuric	Tartaric	Sulfuric	Tartaric	Sulfuric
Untreated	562	536	-	-	-	-
2 hrs PEPCON Recycle	5.0	*	-	-	6.30	-
3 hrs PEPCON Recycle	5.0	*	-	-	6.40	-
4 hrs Holding Tank	5.0	*	-	-	3.70	-
4 hrs + UV	-	-	-	0.022	0.22	0.031
5 hrs Holding Tank	-	-	<0.01	-	0.283	-
5 hrs + UV	-	-	0.275	0.076	0.04	0.212
5 hrs + UV + 6-14 Mesh Charcoal	-	-	0.129	0.076	0.05	0.295
5 hrs + UV + 50-200 Mesh Charcoal	-	-	0.036	<0.01	0.018	0.050

*End Point Masked by Silver Chloride Precipitate

TABLE A-8
Copper Plating Waste Treatment
3% NaCl

<u>Treatment Description</u>	<u>CN⁻ Concentration (mg/l)</u>		
	<u>Titration</u>	<u>Colorimetric</u>	<u>Electrode</u>
Influent (untreated)	525.0	-	-
PEPCON - 1 hour	12.5	-	-
PEPCON - 2 hours	-	0.020	0.005
PEPCON - 3 hours	-	0.008	0.003
PEPCON + Holding Tank (3 hrs)	-	0.028	0.003
PEPCON + Holding Tank (4 hrs)	-	0.052	0.004
PEPCON + Holding Tank (4 hrs) + UV Radiation	-	0.800	0.024
PEPCON + Holding Tank (4 hrs) + UV + Charcoal	-	0.090	0.028
PEPCON + Holding Tank (4 hrs) + Charcoal	-	0.048	0.007

TABLE A-9
Effects of Reaction Time
in Holding Tank

<u>Treatment Description</u>	<u>CN⁻ Concentration (mg/l)</u>	
	<u>Colorimetric</u>	<u>Electrode</u>
Holding Tank - 3 hours	0.028	0.003
Holding Tank - 4 hours	0.052	0.004
Holding Tank - 6 hours	0.122	0.025
Holding Tank - 24 hrs	0.380	0.125
Holding Tank - 48 hrs	0.490	0.180

Samples were taken from the holding tank at several different times and analyzed for cyanide. The data, shown as Table A-9, show an increase of cyanide with time. Cyanide complex breakdown and/or the partial reversal of chemical reactions are possibly the cause of this increase.

UV, Temperature, Activated Carbon and pH

A study was made to determine the effects of activated carbon, temperature, and UV light as a function of pH on the treated effluent from the prototype system. The pH levels used were 3, 7, and 11. The pH of the samples was adjusted prior to the tests involving temperature variations, UV light exposure, and carbon adsorption. The samples analyzed for temperature effects were left for two hours at the test conditions and analyzed. The samples treated by UV light and activated carbon were passed through the UV unit or the carbon columns at a subscale flow rate that would be equivalent to 0.5 gpm flow rate of the prototype system. Samples were taken at 15 and 60 minute intervals. The data from these experiments are given in Table A-10.

TABLE A-10

Effect of UV, Activated Carbon, Temperature and
pH on Cyanide Treatment Prototype Effluent

Prototype Test Date	Prototype Effluent*		Test Conditions				Final Effluent (mg/l)	
	CN ⁻	(mg/l) CNO ⁻	pH	Temp (°F)	UV	Activated Carbon F-200 F-6-14	CN ⁻ (Colorimetric)	CNO ⁻
16 May 74	0.54	85.7	3.0	100			0.21	6.3
			3.0	120			0.20	15.0
			7.3	100			0.46	4.2
			7.3	120			0.18	11.0
			11.0	100			0.35	11.0
			11.0	120			0.41	11.0
22 May 74	0.13	4.0	3.0	100	15 Min		0.159	23.0
			3.0		60		0.146	11.0
			7.0		15		0.215	4.0
			7.0		60		0.120	9.0
			11.0		15		0.185	9.0
			11.0		60		0.175	8.0
23 May 74	0.30	13.0	3.0	100	15 Min		0.095	8.0
			3.0		60		0.101	8.0
			7.0		15		0.195	0
			7.0		60		0.185	0
			11.0		15		0.095	22.0
			11.0		60		0.105	25.0
23 May 74	0.30	13.0	3.0	100	15 Min		0.050	19.0
			3.0		60		0.047	8.0
			7.0		15		0.178	4.0
			7.0		60		0.125	4.0
			11.0		15		0.125	0
			11.0		60		0.125	34.0

*Influent: Cadmium Strip

APPENDIX B

INTERFACE OF THIOKOL WASTE TREATMENT SYSTEM WITH HILL AFB PLATING FACILITY

The flow schematic shown in Figure B-1 shows the interface between the Thiokol system and the Hill AFB plating facility.

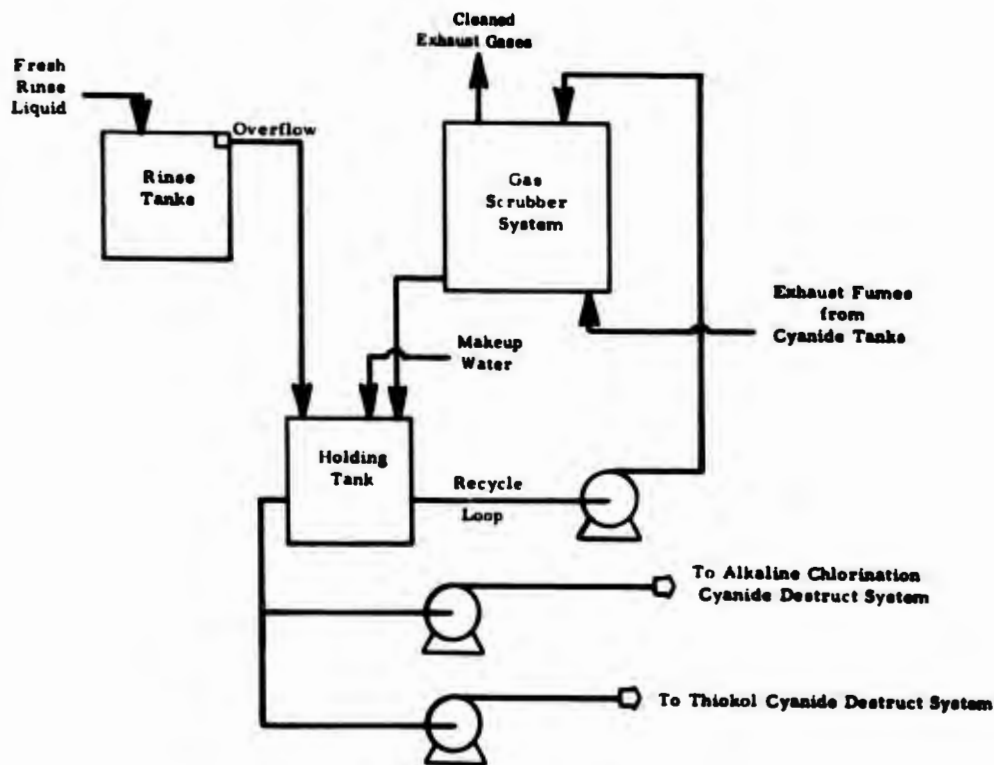


Figure B-1. Thiokol Cyanide Waste Treatment System
Interface Point With Hill AFB Plating Facility