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**CYANIDES: DECOMPOSITION
AND DETERMINATION**

I. GILATH and L. COHEN

Israel Atomic Energy Commission

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I. Gilath and L. Cohen

ABSTRACT

Different cyanide destruction methods such as electrolysis (with and without the addition of salt), hypochlorite treatment and ion exchange detoxication were evaluated on a laboratory scale using model solutions. Parameters were determined for the optimal operation of the investigated processes. Analytical methods were adapted for concentrations and compositions of interest. An easy and rapid method of complex cyanide breakdown by ion exchange treatment was developed for analytical purposes.

1. INTRODUCTION

The effluents of the plating industry contain cyanides of varying composition and concentration. Cyanides in solution can be found as free cyanide ions or complexed with metals as complex anions. The maximum allowable cyanide concentration in an effluent being discharged into a sewer should be less than 0.05 ppm, according to the U.S. Public Health Service regulation. This explains the interest and the great number of works published, concerning various problems of cyanide destruction and analysis.

The aim of the present work was to evaluate different methods for the decomposition of simple and complex cyanides at various concentrations in aqueous solution. Methods published in the literature were tested experimentally and ranges of optimal operating conditions were defined. Analytical methods for the determination of simple and complex cyanides were adapted for dilute and concentrated solutions.

2. SIMPLE AND COMPLEX CYANIDE DESTRUCTION

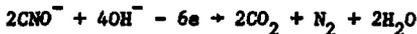
2.1 Electrolytic decomposition of cyanides

The electrolytic decomposition of cyanides has been studied for more than 20 years (1). The reaction conditions on which the

decomposition is based are high temperatures and insoluble anodes. The reactions at the cathode for copper cyanide, as an example, are^(2,3,4):



and at the anode:



In solution the cyanate ion hydrolyzes:



The parameters influencing the electrolytic decomposition are described below. The electrolysis is a lengthy process. It depends on the quantity and initial concentration of the solution, current density at the electrodes, type of electrodes, temperature and mixing. An example can be cited⁽³⁾ : a batch of 7 m³ of a very concentrated dip (about 75 g/l cyanide) was decomposed during three weeks at a current density of 7 A/dm² with carbon steel electrodes. The removal of cyanide was almost linear with time, until the cyanide concentration was

reduced to less than 1 g/l. At low concentrations the decomposition proceeds very slowly. Sometimes heavy scaling of the electrodes occurs. Replacing the anode plates permits further decomposition, but scaling usually recurs in a short time⁽³⁾.

Other metals were tested for greater resistance to corrosion. The electrochemical oxidation of cyanide on platinum electrodes⁽⁵⁾ was investigated by means of voltametric, chronopotentiometric and galvanostatic studies. The proposed mechanism for the oxidation reaction involves the formation of a platinum oxide film which is destroyed and poisoned by the cyanide ion, thus inhibiting the oxidation⁽⁴⁾.

Stainless steel electrodes are less attacked at lower cyanide concentrations, but the rate of destruction of cyanide is quite low.

Graphite electrodes are attacked slightly, the weight loss being about $0.5 \text{ mg/cm}^2/\text{h}$ at 3A/dm^2 . Approximately 5-7 kWh are used to destroy 1 kg CN⁽⁴⁾. Graphite was used also in large scale continuous electrolysis⁽⁶⁾. It has a very high chemical resistance but a high overvoltage for the oxygen evolution is not necessary in the electrolytic oxidation process. Additional details about electrode material can be found in Lurie's work⁽⁷⁾. It may be concluded that the most widely used electrodes are made of carbon steel and graphite.

Higher temperatures favor cyanide decomposition. The resistance of the cell decreases with an increase of temperature, and the voltage required to pass a given current is also decreased⁽⁴⁾. The best

electrolysis results can be obtained at temperatures in the range of 50-90°C.

The rate of cyanide destruction is approximately proportional to the current density (expressed in amperes per unit surface of the electrodes). Dart⁽⁴⁾ studied a wide range of current densities, 0-10 A/dm², but found that 3-4 A/dm² is satisfactory^(4,7,8). The distance between electrodes influences the efficiency of the electrolysis, and depends on the overall geometry of the cell. The experimental results show that a distance of 2-3 cm gives good results. However, in commercial cells, electrodes may be spaced very close together: 1/4 to 1/2 inch. With this spacing it is possible to produce 1000-2000 A by applying 3-4 volts per cell. The obtained current density is 10-50 A/dm² (9,10).

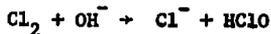
The effect of the anode:cathode area ratio is also an important factor but not critical. Experiments were performed for 1:1, 2:1, 3:1, 4:1 and 5:1 anode:cathode area ratios⁽⁸⁾. Best results were obtained for 1:1 and 2:1 ratios. Considering that the anode surface which faces the cathode is the most effective, the above results are understandable.

2.2. The alkaline chlorination of cyanides

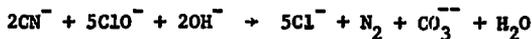
Experiments indicate that the rate of destruction of cyanide during electrolysis decreases markedly when the concentration of cyanide falls below 2 g/l. Therefore, it would probably be uneconomical in practice to use this method for the complete destruction of cyanides. Residual cyanides would have to be destroyed by alkaline chlorination,

which can be achieved by the direct action of chlorine, hypochlorite or salt added during electrolysis.

Chlorides in aqueous solution produce active chlorine during electrolysis. The reactions can be summarized as follows⁽⁶⁾:



The hypochlorite formed by electrolysis reacts with the CN^- :



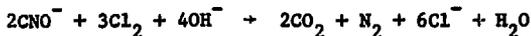
The optimal salt concentration as found by Ruml⁽⁸⁾ is 20-30 g/l and the power consumption is 12-40 kWh per kg CN. The overall reactions were summarized by Ruml⁽⁸⁾

at the cathode:

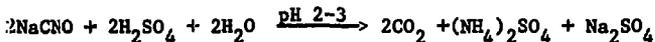
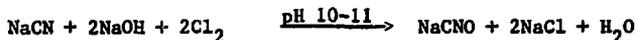


at the anode:



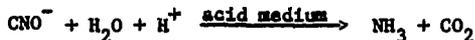


Chlorine can also be added directly by purging gas into the solution, without electrolysis. Cyanide is destroyed by a two-stage oxidation⁽¹¹⁾:



The acid solution is neutralized by the addition of alkali to precipitate the heavy metals and the precipitate is then pumped to the incinerator. The cost estimate presented for the destruction of one pound of CN^- is \$1 (1974). Ten cubic feet of natural gas is burned per pound dry weight of solids in the incinerator⁽¹¹⁾.

Direct addition of hypochlorite to cyanide wastes is widely recommended in the French industry⁽¹²⁾. The hypochlorite is easier to manipulate than chlorine gas, and can be used by unskilled workmen. It is believed that the reaction follows the following mechanism:



At pH 10-11 no chlorocyan (ClCN) is formed and at pH 9-11 there is no danger of chlorine derivatives formation by any form of chlorination. The cyanate formed by chlorination can be destroyed in about five minutes by acid hydrolysis. At pH 8-8.5 it may take about an hour. At pH 10 it may take several hours⁽¹³⁾. A cost estimate was made for the oxidation of 1 lb NaCN to NaCNO and its decomposition by acid hydrolysis, and found to be about \$0.33 (1969). An automated hypochlorite treatment plant for cyanide destruction is described in the work of Ferves Fillela⁽¹⁴⁾.

In a German patent⁽¹⁵⁾ data is found on continuous electrolysis of low cyanide content waste (200 ppm) with added hypochlorite.

2.3. Ion exchangers in cyanide treatment

Ion exchangers are insoluble materials which carry reversibly exchangeable cations or anions. The exchange is theoretically stoichiometric and the capacity of the resin can be expressed in meq/ml resin. The breakthrough capacity, used in column operation, is less than the theoretical value, and depends mainly on the flow rate of the eluent through the column. Ion exchange treatment of cyanide wastes accomplishes the following:

- a) Removes the cyanides from a large volume of dilute wastes and recovers the cyanide, after regeneration of the resin in a concentrated and marketable form (if desired).
- b) Recovers metals from the plating wastes in the concentrated industrial effluents. This is more economical than the precipitation of metals and settling of slurries.

According to the purpose, anionic exchangers or anionic and cationic resins linked in series are used. Ion exchange resins do not destroy cyanides. They merely detoxicate wastes; further treatment of the concentrated effluents is needed. The detoxicated industrial effluents cannot always be recycled, because their salt content is sometimes elevated, when the heavy metals and the cyanides are exchanged for the cation and the anion, respectively, of the resins (sodium as cation and chloride or sulfate as anions). This problem can be solved if resins are in the H^+ or OH^- form, but this is not always economical. Cyanides were successfully absorbed on strong base resins⁽¹⁶⁾. The ion exchange process is particularly attractive for gold cyanide waste solutions, where concentrations are low. It was demonstrated that the strong base resin Amberlite IRA-400 absorbs cyanide without leakage. For the sorption cycle the resin was regenerated with a 5% sulfuric acid solution, and washed with water. The resin was loaded with a 300 mg/l cyanide solution at a flow rate of 0.3 bed volumes per minute. The acid eluent decompose and absorbed complexes and the released metal cations could be further absorbed on a cation exchange resin. It was observed that the free cyanide absorption properties of the strong basic resin are greatly enhanced by impregnation with cuprous cyanide. It appears that the free cyanide combines immediately with the cuprous cyanide and therefore no leakage occurs. A combined flow sheet for cyanide recovery⁽¹⁶⁾ contains an ion exchange column for complexed cyanide, another impregnated with $CuCN$ for free cyanide and a bed for cation absorption. A fourth bed can be added in OH^-

form if the cation exchange is in H^+ form. The four resin beds remove all ions from the waste water.

In U.S. patent No. 3,788,983 ⁽¹⁷⁾ Fries claims "that the only commercially acceptable technique is the complete removal of all ions by ion exchange, however, this technique is not generally applicable because it is low capacity and large chemical usage for regeneration purposes". The essence of this work is the use of ferrous ion as a complexing agent with subsequent adsorption of the soluble complex on a weakly basic ion exchange resin. The ferrocyanide complex is extremely stable. The resin is regenerated with 1-10% NaOH and the concentrated effluent of $Na_4Fe(CN)_6$ can be marketed. In the patent, Fries claims to reduce cyanides to levels substantially below 1 ppm.

Another flow sheet for rinse water (recycling) through ion exchangers is presented in the French journal Galvano ⁽¹⁸⁾. Some problems are encountered in the proper functioning of ion exchange beds. Organic substances used to lower surface tension and break solvent emulsions (from metal degreasing) inhibit the function of ion exchangers. If the pH is not controlled, some metals flocculate as hydroxides which obstruct the flow through the resin.

Metals such as copper, zinc, nickel and cadmium can be recovered from spent cyanide wastes on strong cation exchangers ⁽¹⁹⁾. Considerable interest is currently being shown in heavy metal concentration in waste waters because of their high cumulative toxicity. An elaborate account of heavy metal occurrence, toxicity and detection can be found in P. Chermisinoff's work ⁽²⁰⁾.

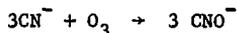
2.4. Other methods of cyanide destruction

Electrolytic oxidation with or without chlorination, hypochlorite treatment and ion exchange detoxification of waste waters are among the most widely used processes. A brief description is given here of some other methods, as well as new trends in this field.

Grace Davison Chemicals of Baltimore developed an ozonizer for the treatment of waste water containing cyanides. Ozone is a stronger oxidant than hypochlorite. Its use is justified when excessive chlorination should be avoided. The oxidation reactions are:



or



The cyanate is further hydrolyzed.

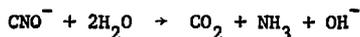
Another oxidation process is the catalytic burning of cyanide-containing wastes. In this process the effluents are acidified to pH 2.5 to liberate the cyanhydric acid, which is removed with an air purge. The gas mixture is burned to $\text{CO}_2 + \text{N}_2$ in a packed column containing a catalyst.

Some variations of this method are already in use. The cyanide solution is injected as a spray, instantly dried and burned. The metals are recovered as oxides. A flow sheet of the catalytic burning of cyanides is given in Galvano ⁽¹⁸⁾ and the approximate price is 3 francs per kg CN^- (1971).

An incinerator for burning residual oil and chemical wastes was installed in Munich (21). It consists of an horizontal barrel kept at 1300° - 1400°C to avoid explosion when burning hydrocarbons. Initially, great difficulties were reported when burning the blend of various residues. A 30% cyanide solution was sprayed into the furnace. In the Munich-type incinerator the cyanide is completely oxidized after 6 hours of burning.

The highly automated disposal of hazardous waste (22) by incineration at Pontypool (U.K.) has a treatment capacity of 50,000 tons/year; the building cost was £ 750,000 (1974).

The Air Liquide Soc. of Paris developed a method of total destruction of cyanides with Caro's acid (monopersulfuric acid). With stoichiometric amounts of acid to cyanide, the following reaction occurs



With excess of acid:



The hydrolysis of cyanate is slow in alkaline media but fast at low pH. The rates of decomposition of various complex metal cyanides by Caro's acid are given in a recent publication of Galvano (12).

Industrial waste regeneration applying dialysis, electrodyalysis or reverse osmosis techniques are still in the development stage.

These techniques recover concentrated solutions and depleted water, thus avoiding the need for cyanide destruction or the high cost of regeneration with ion exchangers or salted effluents (23,24).

A new German patent (25) claims to convert cyanide wastes to an innocuous material by reaction with a formaldehyde solution, which produces ammonia and glycolic acid salts.

Some data and the description of a fully automated effluent treatment plant (1972) is given in Kelsey's report (26).

As described above, many attempts have been made to improve and economize the process of cyanide destruction. Concentrated wastes are most economically destroyed by electrolysis combined with chlorination. For dilute solutions or rinse waters the alkaline chlorination or hypochlorite treatment is more economical. Cyanide wastes can be detoxicated by passing them through ion exchangers. After regeneration, the concentrated cyanides in the effluent need further treatment.

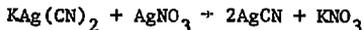
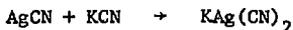
3. ANALYTICAL METHODS FOR THE DETERMINATION OF FREE AND COMPLEX CYANIDES

Cyanides may be present in solution as the free ion (CN^-) or may be complexed with metals and hydrogen. The chemical effectiveness of the free fraction of the cyanide depends on the overall composition of the solution, pH and actual concentration of free and dissociated cyanide ion. Hydrogen ion forms the weak undissociated acid HCN. The greater the hydrogen ion activity, the greater the amount of weak

acid. At pH 8, less than 10% of the cyanide is free; at pH 9.2 50% is free and at pH 12 virtually all the cyanide is in the form CN^- . Transition and heavy metal ions form stable complexes where the cyanide ion is bound. Because of the complexity of the cyanide compounds their estimation is difficult and many methods were elaborated for their determination.

3.1. Determination of simple free cyanides by silver nitrate titration

The Liebig titration continues to be one of the basic procedures for estimating cyanides. Several methods are in use for determining the end point, including turbidity and color of the complex in the presence of iodide ion or silver electrode. The reactions are the following:



In the presence of KI and chlorides, the end point is clear. Sensitivity is about 5 ppm.

Two possibilities have been proposed for the separation of cyanide from materials which interfere with titration : solvent extraction and distillation. Solvent extractions were discontinued because of the emulsifying tendencies encountered with alkaline solvent-water mixtures.

3.2. Distillation procedure

The distillation method consists of releasing the cyanide from an acidified solution and trapping it in an alkaline solution. Simple cyanides are easily distilled from acidified solutions containing interfering substances. Double complexed salts, however, are sometimes quite stable and it is difficult to recover the cyanide freed by acid breakdown and distillation.

The Serfass reflux and the tartaric acid distillation procedures are those most widely used. The apparatus and the methods are described in detail in "Standard Methods" (27). The reflux procedure is more complicated than the tartaric acid distillation, but the former is preferable since it results in a higher recovery of the cyanide. Several difficulties in the distillation were reported (28). The absorption of the distilled hydrogen cyanide in the alkaline solution is not always complete and depends on the heating rate of the distillation, carrier velocity and alkaline absorption facilities. A few hours of distillation may be required to break down some stable complex cyanides.

Goulden (29) reports the recovery of nanogram quantities of cyanide by modifications of the standard methods (27). The modifications were needed because HCN distilled from the solution but was not well absorbed in the alkaline solution.

3.3. Estimation of microquantities

By conversion of cyanide to cyanogen chloride with Chloramin T

solution and reaction with a mixture of pyridine pyrazolone reagent, Epstein (30) was able to form a blue dye which is stable at 25°C for about 30 minutes. The dye follows the Beer-Lambert law between the limit of 0.2 and 1.2 micrograms per ml cyanide ion. This method is both sensitive and reliable.

The above method was also mentioned by Ludzak (28) and compared with another colorimetric method for cyanides, the benzidine-pyridine test.

3.4. The Orion cyanide ion activity electrode

The cyanide electrode⁽³¹⁾ develops a potential proportional to the logarithm of the activity of the free cyanide ion in the sample solution. Its recommended operating range is 10^{-3} - 10^{-5} M CN^- . The electrode life is estimated as 200 h for 10^{-3} M solutions. At higher concentrations it deteriorates rapidly because of the corrosion of the sensing element. With frequent calibration, measurements should be reproducible to $\pm 15\%$ of the cyanide ion activity of the sample solution. If measurements of total cyanide concentration are required, an estimate is made of the total ionic strength and cyanide level, to obtain the recommended sample dilution factor. Then comparison is made with similarly diluted pure NaCN standards.

3.5. Other methods

Bowen⁽³²⁾ described a radiochemical method for determining cyanide and Teske⁽³³⁾ a new potentiostatic measuring procedure. Spot tests, a qualitative test and some other practical methods are given

in "Analysis of Metal Finishing Effluents" (34). Sulfide ion is known to interfere considerably with cyanide determinations. The first simultaneous determination of cyanide and sulfide ions by direct current polarography was reported by Canterford (35).

We would also like to mention Hilbert's report (36) because it gives a method for the determination of cyanate which rarely appears in the analytical literature.

4. EXPERIMENTAL

The purpose of the present experimental work was to compare different methods of cyanide destruction as well as methods of free and complexed cyanide analysis. All the experiments were carried out on model solutions.

4.1. Electrolysis

Laboratory tests of electrolysis were performed in a covered glass container of 12 cm diameter and 15 cm height. The lid was provided with a special arrangement for changing the electrodes and the distance between them. Also, a reflux condenser was attached in case of possible overheating and an opening was provided for temperature recording and sample withdrawal. The container was heated and its contents agitated with a magnetic stirrer. Power was supplied through a current rectifier and current and voltage were recorded. The variable current rectifier also made it possible to experiment with changing the current density.

4.2. Ion exchange

The Amberlite IRA-400 (Fluka) resin was employed in ion exchange experiments. The dry resin (20-50 mesh) was soaked in distilled water and the swollen wet resin transferred to a 3 cm diameter glass column having a glass wool support. By eluting it with an appropriate solution, the resin can be obtained in the desired anionic form. For analytical purposes the resin was transferred to a small diameter column, i.e. a burette.

4.3. Preparation of standard cyanide complex solutions

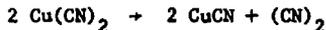
The cyanide complexes were prepared in solution by accurately weighing simple insoluble cyanides and dissolving them in known concentrations of NaCN or KCN solutions. As an example:



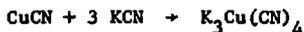
Where simple cyanides were not available, they were prepared. As an example:



The blue CuSO_4 solution gives a yellow Cu(CN)_2 precipitate which is washed and dried. During drying, the precipitate turns white according to the reaction:



The dried precipitate is weighed and transformed to a complex according to:



The prepared solution had the following composition:

12.23 g/l Cu
13.27 g/l Na
20.00 g/l CN^- complexed
1.5 g/l CN^- free
7.05 g/l CO_3^{--}

4.4. Hypochlorite solutions

Two dilute hypochlorite solutions (household bleach) were checked for active chlorine by the standard method for liquid bleach (Scott). The I_2 which is liberated from excess KI by the hypochlorite is titrated with standard thiosulfate solution. The concentrations obtained were 12.7 g/l for the dilute and 18.08 g/l for the x2 solution. Undiluted commercial hypochlorite solutions can be obtained with 120-130 g/l available chlorine.

5. RESULTS AND DISCUSSION

5.1. Free and complex cyanide analysis

The Liebig titration method gave good and reproducible results. The sensitivity of the determination with 0.1 N AgNO_3 is 0.5 mg CN^- per sample or about 5 ppm. Greater sensitivity can be obtained with 0.01 N AgNO_3 solutions. For lower concentration, i.e. 0.1-1.2 mg CN^- /l,

the colorimetric method, using chloramin T and pyridine pyrazolone, was employed. The optical density of the colored cyanide complex was determined at 630 m μ with a Bausch and Lomb spectrophotometer. By plotting the optical density against the concentration of a prepared standard cyanide solution, a linear dependence was observed in the range of 0.1 - 1.2 mg/l. The determination is reproducible. The ultimate sensitivity is about 0.05 ppm.

The determination of complex cyanides by the Serfass or tartaric acid distillation did not give the expected results. Only 80-85% of the added complex cyanide was recovered. The results were not improved by changing the conditions of the acid distillation such as the heating rate, carrier rate, concentration of the alkaline solution, dispersion of the distilled acid and sealing possible leaks in the system.

It was observed that the complex cyanides of Cd and Zn can be directly titrated like simple cyanides. The complexes $\text{Na}_2\text{Cd}(\text{CN})_4$ and $\text{Na}_2\text{Zn}(\text{CN})_4$ are probably not very strong or stable complexes. During the titration, Zn and Cd ions are liberated from the complex and cause turbidity before the end point. The turbidity is caused by $\text{Cd}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$, respectively. By adding NH_4OH , the turbidity disappears because ammonia forms soluble complexes with the above hydroxides. The titration is then completed without difficulty. A confirmation of the possibility of direct titration was found also in Ludzack's work (28).

The complex cyanides of copper, silver, iron, cobalt, etc. cannot be titrated directly because the cyanide is strongly bound in the central anion. For the complex cyanides a new method was elaborated which gave very good results. The simple or complex cyanides are quantitatively absorbed on an anionic resin. When eluting with an acid, the complex is broken, all the cyanides are washed out and trapped in an alkali solution. They can then be evaluated by any standard method. A (20-50) mesh Amberlite IRA-400 resin was used, after washing it with dilute NaOH and water, giving it the hydroxide form. A glass column 1 cm diam, 7 cm height was filled with 5 ml wet resin. A known quantity of complex cyanide (about 25-100 mg/sample) was filtered through the resin bed and the effluent was collected at a rate of one drop per second. The effluent was checked and no cyanide was detected. The resin was then washed with distilled water and the cyanide liberated by two consecutive acid washes: 15 ml 2N H_2SO_4 and 15 ml 4.5 N H_2SO_4 . The first acid elution was performed quickly to avoid the formation and escape of HCN bubbles upward. The second acid wash was performed slowly to complete the total removal of the cyanide. The resin was regenerated after each determination.

We recommend this new method because it is simple and very reliable, and the recovery is complete and reproducible. Absorption of cyanide on the resin and elution take about 15-20 minutes compared to two hours or more with the distillation method.

5.2. The influence of different parameters on the electrolytic decomposition of cyanides

The rate of cyanide decomposition was found to drop during the electrolysis. A typical pattern is shown in Fig. 1.

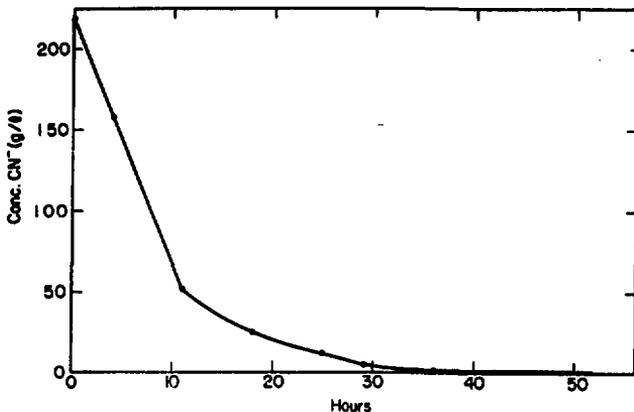


Fig. 1

Rate of cyanide decomposition during electrolysis

Experimental conditions: carbon steel electrode;
cathode area = anode area = 70 cm²; current
density 8A/dm², 90°C

The following experiments were performed changing only one parameter at a time.

- a) The influence of the ratio of the areas of the anode and cathode on the rate of cyanide destruction for 0.6 A/cm² current density, 2 hr time and 90°C temperature, is shown in Table 1

Table 1

Influence of anode : cathode area on cyanide destruction

Anode:Cathode area	% Decomposition
1:1	81.6
2:1	76.8
3:1	67.4
4:1	71.8
5:1	75.5

Best results were obtained for a 1:1 ratio because the most efficient part of the electrode is that part which faces the other. Experimental conditions are given in Fig. 1.

b) The influence of temperature on the rate of decomposition of cyanides at 0.6 A/cm^2 , 90 min, 1:1 electrode area ratio is summarized in Table 2.

Table 2

Influence of temperature on cyanide destruction

Temp., °C	% Decomposition
12	10.3
25	13.8
50	34.8
90	54

It is seen that higher temperatures favor the decomposition; it is thus recommended to work at 90°C .

c) The influence of current density (Table 3) was measured at 0.6 - 2.0 A/dm² and it was found that, as a rule, the current efficiency decreased with an increase of current density. The best results were obtained at 0.7 A/dm² when 99.5% destruction was achieved after 270 minutes.

Table 3

Influence of current density on cyanide destruction

Time, min	% Decomposition			
	5A, 5V	6.8A, 5.5V	9A, 7V	11A, 11V
90	61	74	89	
180	83.2	93	99	89
270	91	99.5		

Unsatisfactory results were obtained at higher current densities because part of the current is lost in water decomposition and other side reactions.

d) The influence of the distance between electrodes, at constant temperature (90°C) and current density (0.6 A/dm²) is summarized in Table 4.

Table 4

Influence of the distance between electrodes on cyanide destruction

Distance, cm	% Decomposition
0.5	55.7
1.5	65.3
2.5	88.9
3.5	77.4

An optimum was obtained at 2.5 cm but this data should be considered only in the context of the overall geometry of the cell.

e) Corrosion of electrodes.

Carbon steel 1020 was subjected to heavy corrosion during electrolysis, especially when complexes were decomposed. Deposits were formed on the anodes and cathode, as well as a thick sludge at the bottom of the cell. A portion of the sludge was analyzed (characteristic Prussian Blue reaction) and found to contain large amounts of iron. The sludge also contained cadmium or zinc according to the complex electrolyzed. It was no use to weigh the electrodes to determine the corrosion, because of the deposits and corrosion products. Electrodes had to be changed before each new batch was electrolyzed.

Graphite electrodes give very good performance, and require much less time and power. For comparison we give the cyanide concentration decrease for graphite and carbon steel electrodes in Table 5.

Table 5
Comparison of graphite and carbon steel electrodes

Time, hr	mg CN ⁻ /ml	
	Graphite	Carbon steel
0	4.15	4.15
1	3.12	3.6
5	0.4	3
6	non-detectable	2.9

Experimental conditions: anode surface = cathode surface = 55 cm²; current: 5A, 5V; 90°C

It can be seen that the time needed for electrolysis with graphite electrodes is much shorter. Only about 25-30% of the initial cyanide concentration was destroyed using carbon steel electrodes, while no cyanide could be detected after the same period of time using graphite electrodes. The power consumption was 30 kW/kg CN^- . Some very finely divided graphite was found in the solution after the electrolysis. After filtration and drying we found that 4 mg/cm² graphite was lost from the electrodes. During repeated operations with other cyanide complexes the performance of the graphite electrodes was equally quick and the graphite loss was even smaller.

5.3. Electrolysis with addition of salt

As was mentioned previously, chloride hastens the electrolytic decomposition of cyanides. $\text{Na}_2\text{Zn}(\text{CN})_4$ was decomposed under the following conditions: 1200 ml solution having an initial concentration of 4.15 mg/ml CN^- was electrolyzed at 90°C, at a current of 5A and 5V with carbon steel electrodes of effective area 2x30 cm² at a distance of 2cm. In the first 12 hours, 62% of the cyanide was decomposed. At this stage, the current generally drops and the process slows down. Here, about 20 g/l salt was added. An immediate increase of current from 5 to 8A was observed and gases evolved. After three minutes 75% of the initial cyanide was destroyed, after 15 minutes 90%, and in less than an hour no cyanide was detected. We note that while heavy corrosion of the electrodes was observed after addition of the salt, the electrolysis time was significantly shortened.

A comparable experiment was performed with graphite electrodes. Since graphite is very efficient by itself and the electrolysis time

is already short, the salt was added at the beginning. A $\text{Na}_2\text{Cd}(\text{CN})_4$ solution of 4.4 mg/ml CN^- was electrolyzed without salt using graphite electrodes with an effective area of $2 \times 55 \text{ cm}^2$ at 2 cm distance and an anode:cathode ratio = 1. Three hours were needed for the complete removal of cyanide. When 20 g/l salt was added to a second identical batch the electrolysis was completed in two hours. The graphite loss was also measured and found to be less than 3 mg/cm^2 electrode.

It can be concluded that graphite electrodes (with or without the addition of chlorides), used in the electrolytic destruction of cyanide, give a quick reaction and show good resistance to corrosion.

5.4. Cyanide destruction by hypochlorite

a) Simple cyanides

When hypochlorite is added to a simple cyanide solution, e.g. NaCN or KCN, gas is evolved, the solution remains clear and no remaining cyanide can be detected. The amount of hypochlorite needed is more than stoichiometric. For a known quantity of cyanide in a sample, increasing amounts of hypochlorite were added until no cyanide could be detected. We found that approximately 2.2-2.5 equivalents of active chlorine are needed to break down one equivalent of cyanide. This finding fits the following reaction mechanism:



This reaction is quick and the cyanide can be determined a few minutes after the hypochlorite addition. Identical results were obtained when cyanide was titrated half an hour later, showing that time is not a factor. Another check of the method was made by adding a known great excess, 10 equivalents, of hypochlorite and back-titrating it with thiosulfate. The hypochlorite consumption was only slightly higher.

b) Complex cyanides

$\text{Na}_2\text{Cd}(\text{CN})_4$ was subjected to hypochlorite action. The same gas evolution was observed as with simple cyanides. The cadmium liberated from the complex flocculated as the white hydroxide. This precipitate can be easily dissolved in ammonia. The quantity of hypochlorite needed was checked by adding increasing amounts, till no cyanide was detected. We needed 2.5 equivalents of Cl^- per equivalent of cyanide. When a great excess of hypochlorite was added and back-titrated, the results were consistent but somewhat higher, about 2.9 eq Cl^- per 1 eq CN^- .

Copper complex $\text{Na}_3\text{Cu}(\text{CN})_4$ was treated with hypochlorite as above. Gas evolved and a black precipitate was formed. The precipitate was filtered, washed, dried and weighed. The amount of copper was calculated and it corresponded accurately to the amount of copper in the sample solution. No cyanide could be detected in the filtrate. A sensitive qualitative test for copper traces was performed on the filtrate. The results were negative, giving additional evidence that all the copper was liberated from the complex and precipitated.

The silver complex $\text{NaAg}(\text{CN})_2$ was also checked. The hypochlorite gave the white AgCl precipitate. It was dried and weighed and the amount of silver corresponded accurately with the initial concentration.

The zinc complex $\text{Na}_2\text{Zn}(\text{CN})_4$ behaved similarly.

It can be concluded that hypochlorite successfully destroys cyanide complexes by precipitating the heavy metal which can then be completely recovered by settling or filtration. No cyanide can be detected in the filtrate. Hypochlorite treatment is recommended for dilute cyanide wastes (as rinse waters) or for relatively small quantities of concentrated wastes, where expenditures for electrolytic equipment, man power and know-how are not warranted.

5.5. Anion exchangers in cyanide treatment

The strong base anion exchanger Ambertile IRA-400, 20-50 mesh, was used. Its capacity is 1.4 meq/ml wet resin. Simple cyanides are trapped as CN anions and complexes are absorbed on the resin in the $\text{R:Me}(\text{CN})_4$ form. The cyanide is liberated from the resin with an anion. The complexes are braked on the resin by an acid and then eluted. The acid effluents are trapped in caustic soda solution.

a) Experiments with simple cyanides

The ion exchange column, containing 30 ml resin, was loaded with 500 mg CN^- . The filtrate was checked and no traces of cyanide were detected, showing that the absorption of cyanide on the resin was

complete. A study of cyanide elution with different concentrations of salt solutions gave the following results (Tables 6-9).

Table 6
Elution with 5% NaCl. Cyanide in resin 500 mg

Successive portions of effluent, ml	20	20	20	20	20	20	20	20
Cyanide, mg	0	3	96.5	238.8	125.7	25	15	1

Total effluent 160 ml. Total cyanide recovered 505 mg.

Table 7
Elution with 10% NaCl. Cyanide in resin 500 mg

Successive portions of effluent, ml	10	10	10	22	22	21	26	22
Cyanide, mg	0	0.5	32	346	97	23	2.5	0

Total effluent 143 ml. Total cyanide recovered 501 mg.

Table 8
Elution with 15% NaCl. Cyanide in resin 300 mg

Successive portions of effluent, ml	Salt solution		Water
	50	50	30
Cyanide, mg	212	75	5

Total effluent 100 ml. Total cyanide recovered 292 mg.

Table 9
Elution with 15% NaCl. Cyanide in resin 800 mg

Successive portions of effluent, ml	Salt solution					Water
	10	11	10	14	25	50
Cyanide, mg	13	198	350	218.5	12.5	4.5

Total effluent 71 ml. Total cyanide recovered 796.5 mg.

As can be seen, when a more concentrated salt solution is used, less eluent is needed for quantitative removal of cyanide. A comparable experiment was performed with a solution of very low cyanide concentration : 4000 ml of 4.75 mg $\text{CN}^-/1$, i.e. 19 mg of cyanide were absorbed from 4 l. The filtrate was free of cyanide. The complete elution of cyanide from the resin at these low concentration needed a large amount of salt solution, about 400 ml 10% NaCl. In practice, regeneration is of no use because a resin can be loaded according to its capacity which is independent of the concentration of the feed solution. Possible break-through of the cyanide through the resin bed should be checked intermittently. The resin also absorbs very concentrated cyanide solutions. As an example, 800 mg cyanide were loaded on the resin from an 88% solution. The filtrate was free of cyanide. The elution was performed with a 15% NaCl solution as shown in Table 10.

Table 10

Elution of 800 mg cyanide from an 88% solution using 15% NaCl

Successive portions of effluent, ml	Salt solution					Water
	10.5	11	10	14	25	100
Cyanide, mg	13	198	350	218.5	12.5	4.5

Total effluent 70 ml. Total cyanide recovered 796 mg.

Other eluents were tried, such as Na_2SO_4 solution. They were not as efficient as salt and 2N NaOH which is a good eluent for simple cyanides. A solution containing 800 mg cyanide was loaded on the resin and the absorbed cyanide was eluted with varying concentrations of NaOH solution, as shown in Table 11.

Table 11

Elution with NaOH. Cyanide in resin 800 mg

Conc. of NaOH	2N	2N	5N	2N	2N	1N	1N	1N
Successive portions of effluent, ml	20	20	30	20	20	20	30	30
Cyanide, mg	100	136	210	200	45	28	24	5

Total effluent 190 ml. Cyanide recovered 748 mg.

It can thus be seen that salt solutions are the most effective for cyanide elution.

b) Experiments with complex cyanides

Complex cyanides are absorbed as the complex anion, $\text{Me}(\text{CN})_4^{-2}$. A strong acid is used to liberate the cyanide from the resin. The acid effluent is trapped in a basic solution. The flow rate of the acid through the resin should be carefully controlled. If the flow rate is too slow, cyanhydric acid will escape upward through the resin.

A solution of $\text{K}_2\text{Zn}(\text{CN})_4$ containing 35 mg cyanide was absorbed. The filtrate was free of cyanide. The resin was eluted with 15 ml 1 N HCl, 20 ml 2 N HCl and finally washed with water. All the effluents were trapped in 40 ml 2 N NaOH. All the cyanide was recovered by titrating the effluent (as free cyanide). Similar experiments were performed with $\text{K}_3\text{Cu}(\text{CN})_4$, $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{KAg}(\text{CN})_2$.

It can be concluded that the strong base resin Amberlite (IRA-400 in our work) efficiently absorbs simple or complex cyanides. Simple cyanides are easily eluted with salt solutions. Complex cyanides have to be broken down by acid and the liberated cyanhydric acid and acid effluent trapped in a basic solution. The cyanhydric acid is neutralized in the basic solution to cyanate which is then either treated further or returned to the plating process. An anion exchange column can be used for decontamination of cyanide-containing solutions, but by itself is not an answer to cyanide decomposition.

6. CONCLUSIONS

The Liebig titration method for free cyanides gave good and reproducible results. The sensitivity is about 5 ppm. For lower

concentrations the pyridine pyrazolone method gave a sensitivity of 0.05 ppm.

A new analytical method was developed for complex cyanide break-down. An ion exchange treatment was found to break down complexes much faster than distillation. The free cyanide in the effluent can be determined by one of the above methods according to the concentration range of the solution to be analyzed.

The use of graphite electrodes was found to be preferable to the use of carbon steel electrodes in the electrolytic decomposition of cyanides. The power consumption for graphite electrodes is about 30 kWh for 1 kg CN decomposed. When salt was added during the electrolysis, the power consumption was about 11 kWh per 1 kg CN decomposed (on graphite electrodes). Cyanide destruction by hypochlorite was also successfully tested. Hypochlorite consumption was about 2.5 equivalents of active chlorine for 1 equivalent cyanide destroyed, i.e. about 3.5 kg active chlorine for 1 kg cyanide. Based on a price of 850 IL/ton hypochlorite solution of 12% active chlorine content, the price of destroying the cyanides by this method is about 25 IL/kg cyanide. Ion exchange resins were found to quantitatively absorb simple and complex cyanides. They can, therefore, be used for on-the-spot removal of cyanides. However, the resins have to be regenerated and the concentrated effluents further treated.

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