
CYANIDE WASTES

Significance

Cyanides are toxic to aquatic life, interfere with normal biological processes of natural purification in streams, present a hazard to agricultural uses of water, and are a menace to public water supplies and bathing. Cyanides exert a toxic action on living organisms, animals, and human beings by reducing or eliminating the utilization of oxygen in a manner similar to asphyxiation. The action at the toxic level is both rapid and fatal.

If the microorganisms in a surface water responsible for proper oxygen balance lose their efficiency or are destroyed, oxygen depletion of the stream ensues. Fish in such a stream stand the chance of being killed either directly by the cyanide content or indirectly by the destruction of the organisms upon which they feed. The toxic threshold level for some species of fish is reported to be 0.05 to 0.10 ppm cyanide as (CN) radical. This toxicity increases as the temperature increases and as the dissolved oxygen decreases. The toxic action is apparently related to photosynthesis, for it has been demonstrated that fish in the absence of sunlight can thrive in water containing 1000 ppm cyanide.

Livestock and other animals are likewise endangered when using a stream polluted with cyanides. Lethal doses to animal and man amount to only 4 mg/lb. of body weight. A stream used for bathing or a domestic water supply should not contain even a trace of cyanide.

Cyanide wastes definitely impair the biological processes of waste treatment plants, although these processes do reduce the cyanide concentration. The amount of reduction of cyanide concentration in these various processes has never been determined, and therefore it is not possible to establish a maximum allowable limit in the raw sewage entering the plant. A maximum of 1 ppm in the raw sewage has been suggested. Most cyanide waste treatment plants discharging into the local collection system are designed to reduce the free cyanide to at least 2 ppm (CN).

In addition to the cyanides present in metal-finishing wastes, there may be copper and zinc ions, which are also toxic to fish and other aquatic life. The toxic threshold level for some species of fish is reported to be 0.10 to 0.20 ppm copper and zinc.

Occurrence

While cyanide compounds are widely used in industry, five processes are responsible for most of the cyanide wastes causing stream pollution and presenting problems in waste treatment plant operation. These processes are: metal plating, case hardening of steel, neutralizing of acid "pickle scum," refining of gold and silver ores, scrubbing of stack gases from blast and producer gas furnaces.

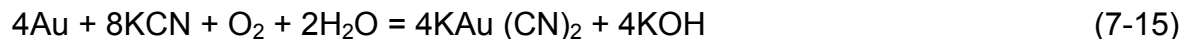
Metal Plating: The greatest source of cyanide-bearing waste is found in the metal-finishing industry, whose electroplating plants are distributed throughout the country. Most of the cyanide wastes are the rinse waters, spillage, and drippings from the plating solutions of cadmium, copper, silver, gold, and zinc. These plating solutions will vary in concentrations of alkali and "free" cyanide (sodium or potassium), but the various metal baths are similar in concentration. The following shows the contents of a solution for a brass-plating operation:

Copper cyanide	4 oz/gal	30000 ppm
Zinc cyanide	1 1/4 oz/gal	9200 ppm
Sodium cyanide	7 1/2 oz/gal	57000 ppm
Sodium carbonate	4 oz/gal	30000 ppm
Total CN =		39000 ppm

Case Hardening of Steel (Nitriding): The process of heat treating steel by cyanide consists of immersing the steel part at a predetermined temperature in a molten bath of a mixture of sodium cyanide, barium chloride, sodium chloride, potassium chloride, and strontium carbonate. When the part has been held for the proper time in this molten bath, it is withdrawn and quenched in a continuous flow of water. The discharge from such a bath may be expected to run as high as 50 to 100 ppm of free cyanide.

Neutralizing of Acid Pickle Scum: In the pickling of steel sheet for the removal of mill scale, the metal is usually dipped in dilute sulfuric and hydrochloric acid. As the steel leaves this pickling bath, a coating called pickle smut, consisting of materials not soluble in the acid - iron carbide, silicon, silicon carbide, copper, and copper sulfides remains on the surface. In addition, ferrous sulfate and ferrous chloride are formed and cling to the surface. If the sheet is then air dried or neutralized with caustic, the ferrous iron is converted to ferric iron, which covers the pickle smut and forms a coating difficult to remove and destructive to the finish of the sheet. It can be removed by agitation in a solution of sodium cyanide (0.2 oz/gal) and sodium hydroxide (0.2 oz/gal). The resulting waste from this solution contains free cyanide in concentrations between 200 and 1000 ppm.

Refining of Gold and Silver Ores: The present method of gold recovery from ore is the McArthur-Forrest process, first patented in 1887, which is based on the solubility of gold in a cyanide solution. The gold is ultimately precipitated from this solution by zinc dust. The chemical reactions are as follows:

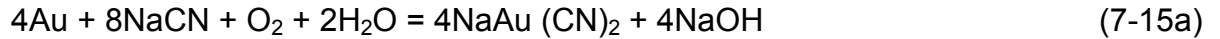


The precipitation of gold by zinc dust is represented by:



The potassium-zinc-cyanide solution remaining after the gold is precipitated in Eq. 7-16 is the waste to be treated.

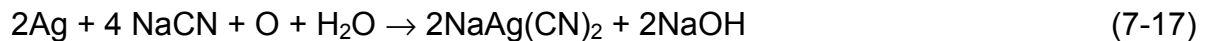
Alternatively, gold can be dissolved in a sodium cyanide solution:



The gold is then precipitated with zinc dust as follows:



The recovery of silver from its ore is similar. The reaction is:



The silver is then precipitated by zinc dust or aluminum powder. The remaining cyanide solution must then be treated for the destruction of cyanides before disposal.

Scrubbing of Stack Gases: Cyanide is a by-product of the manufacture of carbides. The cyanide gets into the flue gas and appears in the wastewater from the flue gas scrubber. This wastewater must then be treated for the destruction of the cyanides.

All of these wastes described above are so toxic to man and animal alike that even in remote areas such as Nevada, where there are many gold and silver processing plants, the state Department of health requires that the cyanide be completely destroyed, even when these wastes are stored in protected ponds.

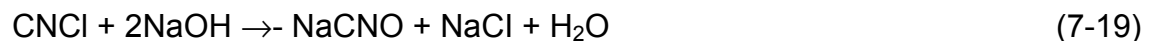
Chemistry of the Treatment

There are two types of cyanide wastes: free cyanide (NaCN or KCN), and combined or complex cyanide ($\text{Na}_2 \text{Au}(\text{CN})_2$).

Destruction of Free Cyanide to Cyanate: When chlorine in its various forms (represented as C12 below) is applied to a free cyanide such as sodium cyanide, oxidation takes place, producing cyanogen chloride:



This reaction is practically instantaneous, and is independent of pH. Cyanogen chloride is also a toxic waste, and, since it volatilizes readily (similar to NCl_3), its formation is to be avoided. Cyanogen chloride can be converted to a more stable compound with proper pH control. In the presence of alkali, represented by NaOH, it decomposes to cyanate at pH 8.5 to 9.0 as follows:



At a controlled pH of 8.5 to 9.0, it takes 10 to 30 minutes for 100 percent completion of this reaction - that is to say, the conversion of free cyanide to cyanate with chlorine. As the pH

increases, the reaction time diminishes. At pH 10 to 11, the time is on the order of 5 to 7 minutes. If the pH drops to as low as 8.0, cyanogen chloride will begin to form. This is to be avoided.

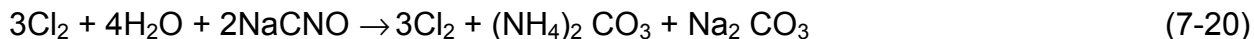
The theoretical requirements for destruction of free cyanides to cyanates are as follows: 2.73 parts of chlorine for each part of free cyanide as CN; 1.125 parts of caustic as, NaOH or 1.225 parts of hydrated lime (Ca(OH)₂) per part of chlorine applied.

In actual practice, it requires more chlorine since other chlorine-consuming compounds are usually present.

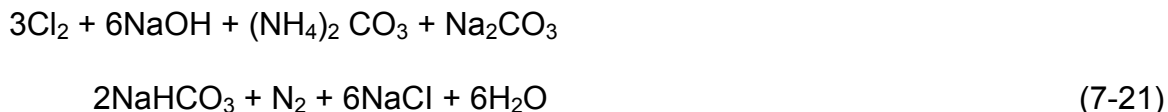
Usually the waste is of rather high alkalinity, and so the alkali requirements average out less than one part - usually 0.6 to 0.8 parts of alkali per part of chlorine. If ammonia is present in the waste, causing formation of chloramines, it is not economically desirable to chlorinate beyond the breakpoint to a free chlorine residual, since chloramines will react to destroy the free cyanide. It simply takes a little longer time. For chloramine treatment, allow an additional 15 minutes. The pH control is critical and is to be measured after chlorination.

Either the flow-through or the batch system of treatment is acceptable when it is necessary only to destroy cyanides to cyanates. The flow-through system can be more economical since it is possible to control the reaction between chlorine and cyanide to form cyanate before the reaction between chlorine and cyanate can begin. This economical advantage may not be of primary consideration when it is imperative always to destroy the free cyanide completely.

Destruction of Cyanates to Carbon and Nitrogen: Cyanates are several hundred-fold less toxic than are the cyanides, but there -are times when it is mandatory to destroy them. The cyanates present as the end product in the destruction of the cyanides at pH 8.5 to 9.0 are not readily decomposed by water or the excess alkali present in the treated waste unless free chlorine is present. The cyanates in the presence of chlorine slowly hydrolyze to form ammonium carbonate and sodium carbonate:"



Chlorine does not take part chemically in this reaction, but does aid in completing the reaction within one to one and a half-hours. It is thought that chlorine acts as a catalyst in Eq. 7-20. The chlorine in Eq. 7-20 must be free available to complete this reaction. After the hydrolysis of Eq. 7-20 takes place, the chlorine and caustic rapidly oxidize the ammonium carbonate to nitrogen gas, and the carbonates are converted to bicarbonates as follows:



As part of this reaction, but not shown, small amounts of inert nitrous oxide (N₂O) and volatile nitrogen trichloride (NCl₃) are also formed.

The complete destruction of cyanides and cyanates to carbonates, nitrogen, and nitrous oxide theoretically requires: 6.82 parts of chlorine per part of free cyanide as CN; 1.125 parts of caustic (NaOH) or 1.225 parts of hydrated lime (Ca(OH)₂) per part of chlorine applied.

In practice, it requires slightly more chlorine to deal with other chlorine compounds, which may be present. Any ammonia initially present will have to be destroyed by the breakpoint phenomenon in order to insure the formation of free chlorine. This requires approximately 10.0 ppm chlorine per ppm of ammonia nitrogen.

The alkali requirements are usually less than one part (0.6 to 0.8) of alkali per part of chlorine, owing to the frequently high initial alkalinity of these wastes.

Either a flow-through or a batch system can be employed for the complete destruction of cyanides. In either case, the minimum holding time for all reactions to go to completion is one and a half-hours. In a flow-through system, short-circuiting becomes critical; therefore it is necessary to monitor the waste at several points, utilizing ORP measurements.

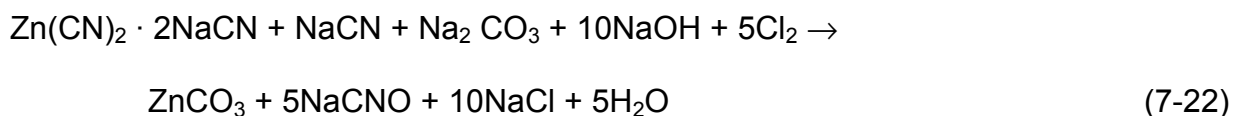
Removal of Metallic Ions In the electroplating industry, the plating baths and rinse waters contain an excess of cyanide above that required to form the soluble metal cyanide complexes. The excess cyanide is called free cyanide; in the complex metallic form, it is known as the combined cyanide. The latter forms can be those of cadmium: Cd(CN)₂ · 2NaCN; of copper: Cu(CN)₂ · 2NaCN; of silver: AgCN · NaCN; and of zinc: Zn (CN)₂ · 2NaCN.

The chlorine and alkali requirement for the destruction of cyanides and cyanates in metal plating is based on the total cyanide present = free plus combined.

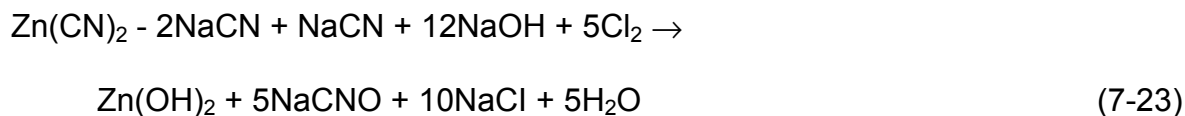
Chlorination of metallic cyanide wastes differs from that of free cyanides as follows:

1. The metals are more or less converted to insoluble oxides, hydroxides or carbonates.
2. These insoluble compounds require additional facilities for sedimentation and sludge disposal.
3. Additional chlorine is required to oxidize certain metals to a higher form, specifically copper and nickel.
4. When nickel is present, it interferes somewhat with the destruction of cyanides to cyanates.
5. When iron is present as ferrocyanide, it is readily oxidized to ferricyanide, which resists destruction by the alkaline chlorine process.

The chlorination of such plating wastes to the soluble alkali cyanates and the insoluble metallic precipitate is shown by the following reaction, which forms the insoluble zinc carbonate:



or by forming the insoluble zinc hydroxide:



The above reactions are rapid in the presence of a free chlorine residual. If chloramines occur, the reaction will not go to completion, and insoluble metallic cyanides may be found in the sludge. This can be avoided by monitoring to a free chlorine residual or to the proper ORP level. The volume of sludge will be on the order of 1 percent of the initial waste when the total cyanide concentration is on the order of 50 to 75 ppm.

When copper or nickel plating rinse waters (which are cyanide free) are mixed with other cyanide wastes and treated, additional chlorine is consumed in converting the cuprous copper and nickelous nickel to higher forms as follows: 0.56 parts of chlorine per part of cuprous copper; 2.25 parts of chlorine per part of nickelous nickel-, 1.125 parts of caustic (NaOH) or 1.225 parts of hydrated lime (Ca(OH)₂) per part of chlorine applied.

Interference by Nickel Nickelous nickel forms a cyanide complex which interferes with the destruction of cyanides to cyanates. It is reported that this complex cyanide cannot be completely destroyed to cyanate in a relatively short time, even in the presence of a free chlorine residual.

However, it creates no problem when the cyanides are to be completely destroyed to carbon dioxide, nitrogen, and nitrous oxide.

In a flow-through plant in which the cyanides are to be converted to the cyanates, the presence of nickel may be solved as follows:

1. Separate nickelous waste from the cyanide waste.
2. Apply nickelous waste to inlet of settling basin along with the cyanide waste after chlorination (nickelous waste does not contain cyanide).
3. Allow the nickelous oxide or hydroxide formed by the reaction with the alkali to settle out. Any excess free chlorine in the chlorinated cyanide waste rapidly converts the nickelous nickel to the black nickelic oxide, which hydrolyzes further to the insoluble hydroxide.

Interference by Iron: Photographic process wastes contain potassium and sodium ferricyanides among other significant chemicals deleterious to the quality of receiving waters. Both ferrocyanide and ferricyanide are toxic to some fish in the presence of sunlight at levels as low as 2 mg/l and therefore should not be discharged without treatment to bodies of water used for beneficial purposes.

While the ferrocyanide is readily oxidized to ferricyanide by chlorine, it does not appear that it can be destroyed directly by alkaline chlorination. It is therefore necessary to decomplex the iron cyanide so that it can be destroyed by chlorine. The addition of mercuric chloride to the waste, to decomplex the iron cyanide, has been suggested. This would form mercuric cyanide, which can

be destroyed by the alkaline chlorination process, but the mercury would then have to be recovered from the waste.

Process Control

The monitoring and control of cyanide destruction to either cyanates or to carbon dioxide and nitrogen require sophisticated laboratory expertise.

For the flow-through or continuous process treatment, the only satisfactory monitoring technique is the use of ORP control. The ORP measuring cell consists of a measuring electrode and a reference electrode (Fig. 7-5). There are two conveniently spaced ORP plateaus in the destruction of cyanides by the alkaline chlorination process. Fig. 7-6 shows the first plateau, where cyanide is converted to cyanates at approximately +400 mv. The complete destruction of the cyanates occurs at the second plateau, some +200 mv higher.

These values are relative, depending on the poise of the waste. For example, the first plateau on some wastes might be as low as +325 mv, and the second at +500 mv. Therefore the poise of the waste must be determined in order to establish the set point of the ORP controller.

If the cyanides are to be converted to cyanates only, then it is necessary to run quantitative tests for cyanides and cyanates to determine the optimum chlorine dosage. It is from these tests that the first plateau of the oxidation-reduction potential is determined.

The following procedures are suggested:

The modified Liebig titrimetric method, for the determination of total cyanide in raw waste and the total residual cyanide in the treated waste, is applicable where great accuracy is not required and where it is not necessary quantitatively to measure the presence of minute quantities of total residual cyanide.

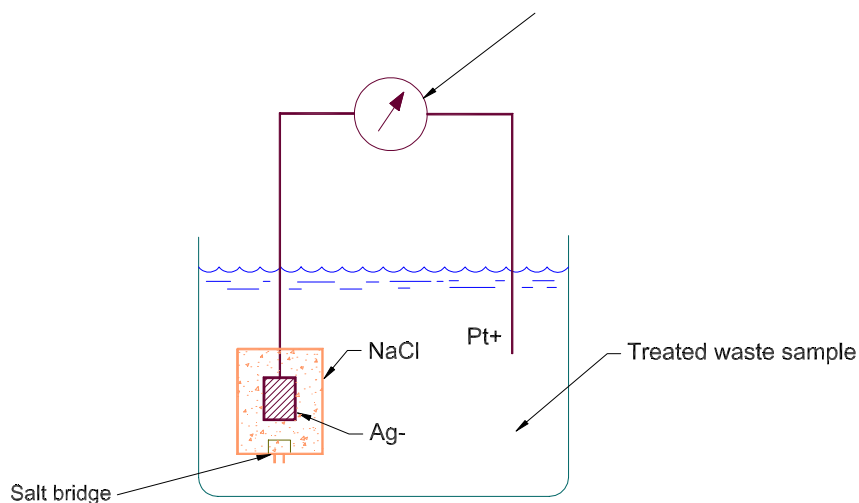


Fig. 7-5 ORP cell for cyanide waste treatment.

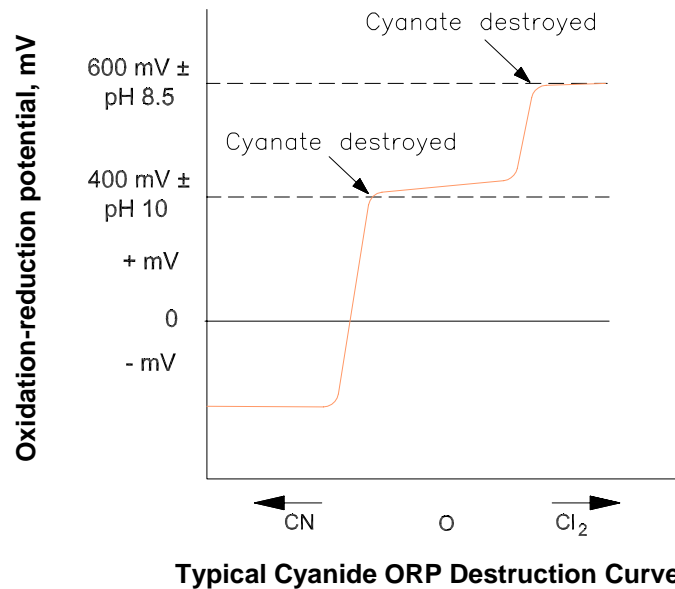


Fig. 7-6. Typical ORP versus cyanide destruction curve.

The pyridine-benzidine method and the pyridine-pyrazolone method can be used for the microanalysis of any residual total cyanide left in the waste after treatment.

A modification of the Herting method is used for determining any residual cyanate left in the waste after treatment.

For the complete destruction of cyanides in a flow-through system, it is necessary to carry a free chlorine residual of 2 to 5 ppm at the end of the required contact time. Measuring the ORP at this residual level will determine the poise of the particular waste and thereby establish the set point of the ORP controller.

It is necessary at all times to be able to determine quantitatively the chlorine residual at the selected control points in the treatment system. This can be done with the acid O -T test or the amperometric titrator. When it is not necessary to distinguish between free and combined chlorine residual, either method is suitable.

For distinguishing between the two forms of available chlorine, only a properly modified amperometric titration procedure is satisfactory. Heavy metal ions, such as cuprous and silver, as well as high concentrations of cupric ion interfere with the amperometric titration. In the complete destruction of cyanide wastes, dichloramine is always present, and the total combined chlorine may amount to as much as twenty-five times that of the free chlorine. It is possible to titrate free chlorine in the presence of up to 25 ppm of monochloramine, but the dichloramine must be less than 5 ppm. The remedy is to apply opposing voltage to make the proper change in the zero point of the ammeter scale on the titrator. This is easily done by use of a 1.5 volt dry cell.

For the batch process control, the following is suggested:

For the destruction of cyanides to cyanates, control to a free chlorine or chloramine residual of 0.2 to 0.5 ppm at pH 8.5 to 9.0 after chlorination.

For the complete destruction of cyanides to carbon dioxide and nitrogen, continued chlorination at a pH not less than 8.5 to 9.0 is required until a free chlorine residual (0.5 to 1.0) is present after not less than one and a half to two hours retention. This would be at the suction side of the circulating pump and ahead of the point of chlorine application.

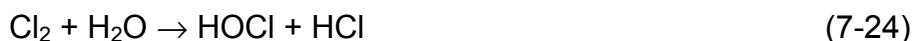
When metallic ions are present, the destruction of cyanides to cyanates also requires the appearance of a free chlorine residual.

Proper laboratory analysis will require dechlorination of the sample and usually distillation as well. These procedures are necessary to prepare the sample for the quantitative estimation of total cyanides and cyanates.

In using chlorinated samples for a total cyanide or cyanate analysis, it is essential (1) to remove any remaining cyanogen chloride before dechlorination by increasing the pH of the sample to 10 to 11 by addition of alkali, preferably NaOH, and (2) remove all residual chlorine by a reducing agent such as sodium sulfite.

Distillation is necessary to obtain the total cyanide in the raw or treated waste when metallic cyanide complexes are present and to separate the cyanide from objectionable turbidity, color, and other substances, which interfere chemically with specific tests for cyanides.

Hypochlorite: If the quantities of cyanide to be destroyed are small enough, it is perfectly acceptable to use hypochlorite. The same amount of available chlorine is required. The only difference is that caustic is not required when hypochlorite is used. The following equations demonstrate why equal amounts of available chlorine are required whether it be hypochlorous acid made from chlorine gas and water:



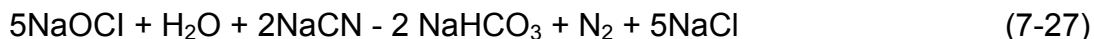
or sodium hypochlorite, which is made from chlorine gas, water, and caustic:



Therefore, using chlorine water:



or hypochlorite:



Chlorination Facility

The first chlorination plant for the destruction of cyanides in the United States was built in 1942. Since that time the alkaline chlorination system has been widely accepted. Some of these installations have been well documented.

Many plant installations operate mainly on the batch method, but utilize automatic pH control and ORP measurement to control the destruction to cyanates. In this form, the individual waste treatment system is allowed to discharge the cyanates directly to the municipal or other waste collection system. In some localities, wastes from individual plants are collected in a tank truck and taken to a central batch treating plant. Other plants, for example, those in areas of automobile manufacturing, munitions manufacturing, and ore processing, may be the sophisticated completely automated flow-through type.

It is customary to recirculate the cyanide waste through the chlorinator injector wherever possible. If a batch system is indicated, smaller, less expensive equipment may be used, whereas in a flow-through system more units of larger capacity may be required since the chlorinator "sees" the waste only once in the flow-through system. In both systems, the water to power the operation of the injector is always that of the waste itself. Fig. 7-7 illustrates a typical batch system.

Let us assume that the cyanides are to be converted only to cyanates. The total cyanide content of the waste is 1500 ppm, and the capacity of the batching system is 5000 gal/day. To convert to cyanates requires a chlorinator capable of delivering 4 ppm Cl_2 per ppm cyanide = 6000 ppm total capacity in 5000 gallons.

$$\begin{aligned} 6000 \times 8.33 &= 49,980 \text{ lb./mg} \\ 5000 \text{ gal} &= 0.005 \text{ mg} \\ 0.005 \times 49,980 &= 249.9 \text{ lb. chlorine required} \end{aligned}$$

A 2000 lb./day chlorinator would be the unit of choice. This unit operating at capacity could treat the entire batch in three hours by recirculating all the waste through the injector, as shown in Fig. 7-7. The caustic feeder should be able to match the 2000 lb. rate of the chlorinator; this would amount to a rate of approximately 313 gal/day, so that the caustic feeder should have a capacity of approximately 350 to 400 gpd.

Theoretically it requires 1.125 parts of NaOH to neutralize each part of chlorine. In practice, because these wastes have such high alkalinities and high pH, it usually requires about 0.9 to 1.0 part caustic per part chlorine. Assume 1.0 part caustic to each part chlorine.

Caustic is usually handled at 50 percent strength. The sg is 1.52, and therefore each gallon of 50 percent caustic = 6.38 lb. NaOH.

$$\frac{2000 \text{ lb. Cl}_2 \text{ per day}}{6.38 \text{ lb./gal}} = 313 \text{ gal/day}$$

The system should have an indicating pH meter. Automatic operation or a time clock system is optional. Confirmation of cyanide to cyanate can be achieved by an indicating ORP unit.

Fig. 7-8 illustrates a completely automated flow-through system. Here the pH is automatically controlled, using a ratio system to provide the proper amount of caustic to the chlorine being fed. In this case, it has been decided that the complete destruction of cyanide to nitrogen and carbonates is required. The success of this system is based on the ORP control and monitoring system. Once the set point of the ORP controller has been determined

by laboratory procedure, described previously, the ORP controller takes over the control and monitoring of the chlorination system. This in conjunction with automatic pH control integrates a completely automatic flow-through system.

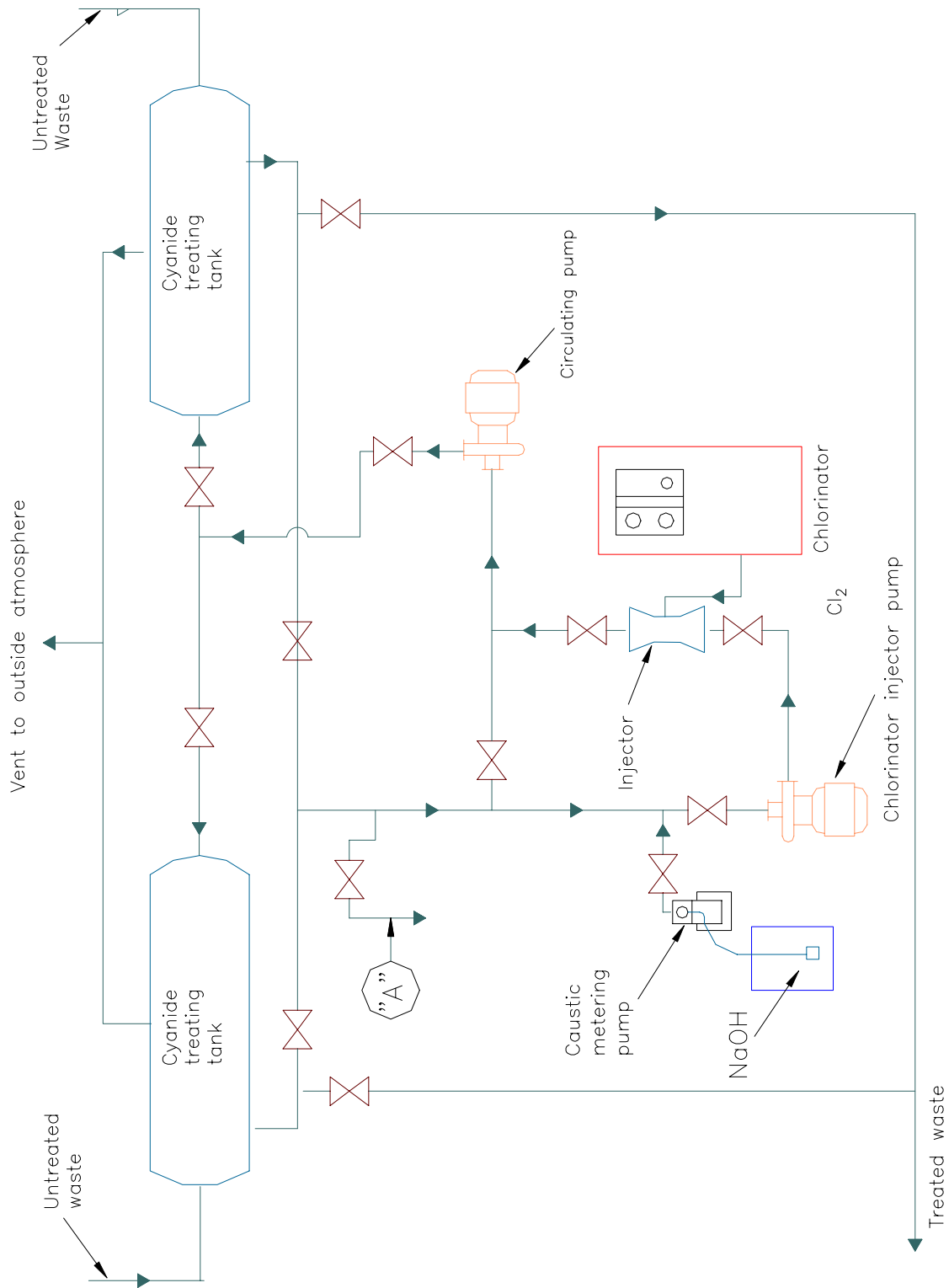


Fig. 7-7 Typical schematic diagram of batch-type chlorination system for the destruction of cyanides. (Free chlorine residual at point "A" denotes complete destruction of cyanates to carbon dioxide, nitrogen, and nitrous oxide.)

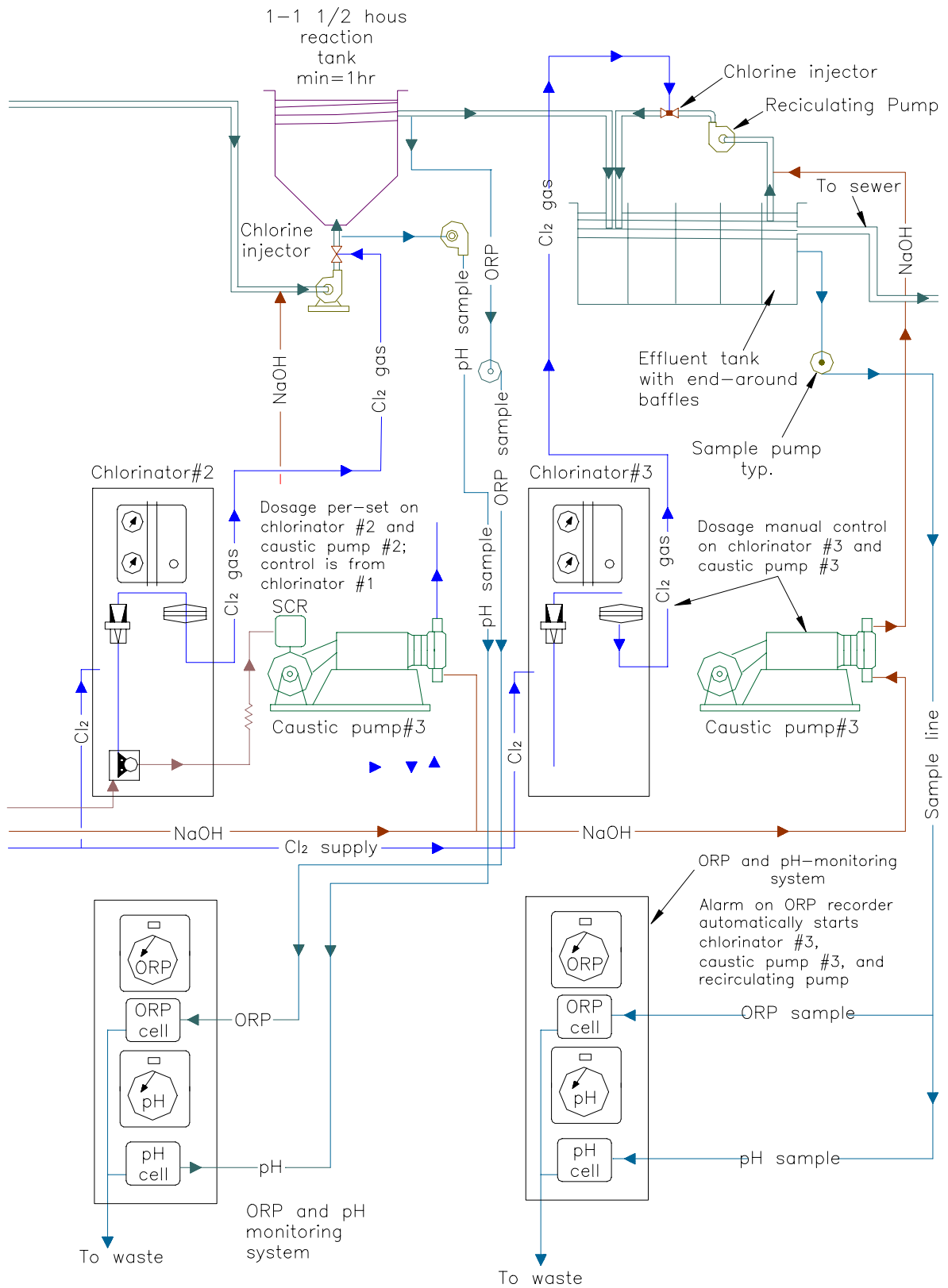


Fig. 7-8 (continued)

Frequent laboratory checks should be made to verify the ORP controller set point as well as the validity of the pH electrodes.

Controlling the Oxidation of Cyanides by the Chlorination Process

The Potential Curve or Characteristic for the Oxidation of Cyanides. When chlorine in increasing amounts is applied to a cyanide-bearing stream, the pH of which has previously been adjusted to 8.5 to 9.0, the potential of the treated waste increases along a characteristic curve similar to that illustrated by Fig. 7-9. The potential levels plotted vary somewhat with the potential cell; therefore the potentials shown in the figure are only examples of the different levels recorded by a representative cell.

Furthermore, it is important to remember that a change in pH affects the potential. A drop in pH results in an increase in potential, while a rise in pH causes a decrease in potential. It is therefore essential for best control that the pH of the raw waste be maintained within reasonably close limits prior to chlorination.

The potential system, for purpose of further discussion, is divided into four potential levels: (1) the reduced or cyanide potential level; (2) the cyanate-chloramine potential level; (3) the free chlorine potential level; and (4) the controlling potential level.

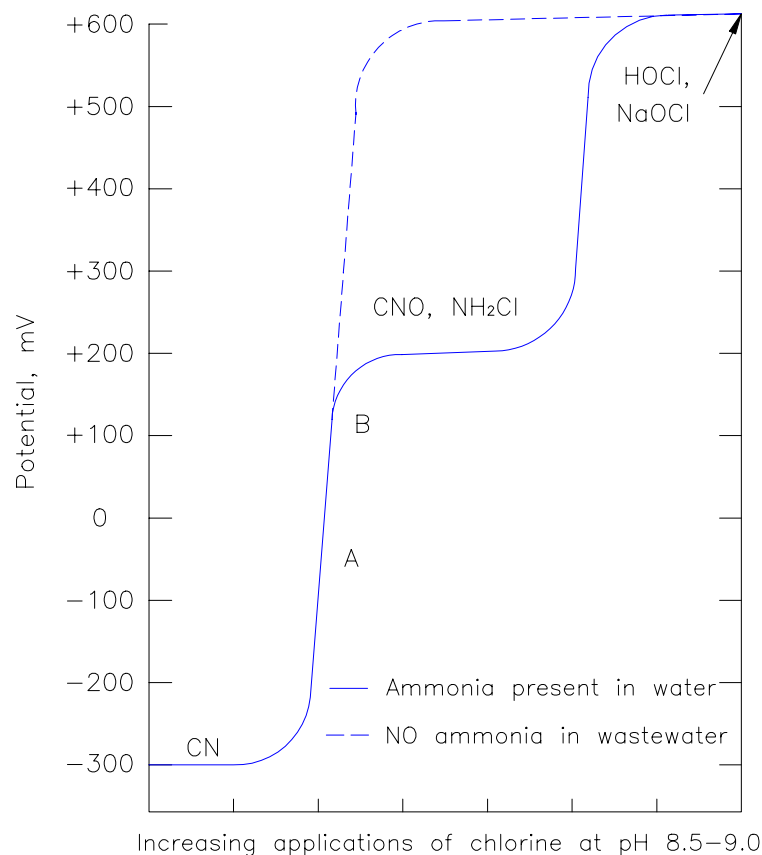


Fig. 7-9. Relationship of potential versus increasing amounts of chlorine in the presence and absence of ammonia in a cyanide destruction system.

The Reduced or Cyanide Potential Level The reduced potential level is the potential level of the raw waste and the raw waste chlorinated with an insufficient amount of chlorine (less than 2.73 parts of chlorine per part of CN). The constituent most affecting the potential is the cyanide. This reduced potential level can therefore also be called the cyanide potential level. In the potential system involved with the chlorination of the waste, it is the lowest potential level.

In Fig. 7-9, the cyanide potential level (-300 mv) is maintained with increasing applications of chlorine until practically all of the cyanide has been oxidized to cyanogen chloride and more than 90 percent of the CNCl, within three minutes, has been converted to cyanates, at which time the potential will have risen to zero or +50mv. Additional retention time, sufficient to complete the hydrolysis of the cyanogen chlorides to cyanates, will result in a higher stabilized potential at the cyanate potential level with no additional chlorine. Up to this point, the presence or absence of ammonia in the raw waste make little difference in the end result. However, as chlorination continues beyond the theoretical 2.73 parts of chlorine to 1 part of CN, the presence or absence of ammonia in the raw waste is of extreme importance.

The Cyanate or Chloramine Potential Level The cyanate potential level is the potential level of the waste chlorinated with just sufficient chlorine completely to convert all of the cyanide to cyanates. As mentioned previously, this level is not reached immediately, since a retention period of thirty minutes or more is usually required to complete the hydrolysis of the last small fraction of cyanogen chloride.

As chlorination proceeds beyond the application necessary to reach the cyanate potential level, which in practice requires a somewhat greater ratio of chlorine to cyanide than the theoretical 2.73:1 ratio, two situations occur: (1) where ammonia is present in the raw waste, and (2) where ammonia is not present in the raw waste.

In the presence of ammonia in the raw waste, any chlorine applied in excess of that required just to convert the cyanide to cyanates appears as chloramine residual. The cyanate and chloramine potential levels are identical, and this level is shown on Fig. 7-9 at about +200 mv. Usually, when ammonia is present in the waste, the cyanate potential level is the highest potential level attained, since it is seldom feasible to convert all of the ammonia to chloramines. However, if enough chlorine is added completely to react with all of the ammonia in addition to the cyanide initially present in the waste, further increases in chlorine application appear as a free chlorine residual, in which case the potential rises to a new maximum at about +600 mv.

When no ammonia is present in the raw waste, any chlorine applied in excess of that required just to convert the cyanide to cyanates appears as a *free chlorine residual*, and the potential rises immediately to a value of about +600 mv, as shown on Fig. 7-9 by the broken curve.

The Free Chlorine Potential Level It has been mentioned that the *free chlorine potential level* may be attained in two different ways, determined by the presence or absence of ammonia in the waste. The solid curve in Fig. 7-9 illustrates the potential characteristic with ammonia present, and the broken curve shows the characteristic when no ammonia is present in the raw waste. Both curves are identical while the first reaction is being completed - namely, the

oxidation of cyanide to cyanogen chloride and the subsequent hydrolysis of this cyanogen chloride to cyanates.

Since oxidation of the cyanates by additional chlorination requires not only the presence of a *free chlorine residual* but also a contact period of perhaps forty-five minutes, the *free chlorine potential level* may be reached momentarily when no ammonia is present by applying more than enough chlorine to complete the cyanate reaction but not enough completely to convert all of this cyanate to nitrogen and carbon dioxide. In this case, the potential will remain at the free chlorine level as the oxidation of the cyanates proceeds until all of the excess free chlorine is used up, at which time the potential will fall to the cyanate level again.

The slowness of this cyanate-free chlorine reaction also accounts for the plateau on the solid curve at +200 mv. in the presence of ammonia which represents the *cyanate-chloramine potential level*, since any excess chlorine applied after the cyanates have formed reacts quickly with the ammonia to form chloramines. Because chloramines will not oxidize the cyanates to nitrogen and carbon dioxide, it is necessary to apply enough excess chlorine to (1) combine with all the ammonia, and (2) to react with all the cyanates before the *free chlorine potential level* can be reached and maintained. Thus the length of the cyanate-chloramine plateau at +200 mv is directly associated with the amount of ammonia present in the waste.

The Controlling Potential Level For purposes of control, it is important to sample the chlorinated waste as soon after the application of chlorine as is possible to obtain a sample which has significance or meaning with respect to the process. In practice, this has been found to be three minutes (the control potential retention period). Point A in Fig. 7-9 represents the midpoint between the *cyanide potential level* and the *cyanate-chloramine potential level* - in this case, -50 mv.

Below this potential, cyanides are likely to be present in increasing small amounts with decreasing small applications of chlorine. Above this potential, a chlorine residual, free or chloramine as the case may be, will be present in increasing small amounts with increasing small applications of chlorine.

With the process under automatic potential control, the potential will at times fluctuate above and below the set point. This raises the possibility of having present small amounts of cyanides in the treated waste at times if the control potential point is set at the no cyanide-no chlorine residual level of - 50 mv.

In view of the axiom that cyanides and a chlorine residual cannot be present in solution at the same time, it appears safer to have any possible fluctuation in the control potential occur in the zone in which chlorine residuals in small amounts will always be present after a three-minute retention period. In the representative cell (Fig. 7-9), such a potential control or set point has been set at B +100 mv.

This controlling potential may be computed as follows:

Formula:

Controlling potential level in mv. = calibrated cyanide potential in mv plus 80 percent of the potential difference in mv between the calibrated cyanide and cyanate potentials.

Example: Calibrated cyanide potential = -300 mv
Calibrated cyanate potential = +200 mv
Potential difference = 500 mv
80% of potential difference = 400 mv
Controlling potential level = -300 mv + 400 mv = + 100 mv

In some cases, it may be possible to calculate this controlling potential level on the basis of a smaller percentage figure for the potential difference. This applies particularly to plants converting only to cyanates and where the 80 percent figure may produce a continuing chlorine residual, which is considered excessive.

In terms of cells other than the representative cell mentioned in this discussion, knowledge of the cyanide and cyanate potential levels for a particular cell can be seen to be of utmost importance. Only from this knowledge is it possible to determine the proper control and alarm points for the individual cells associated with the control system. Normally the calibrated potential levels for individual cells should agree within +50 mv.

If the potential for any cell disagrees beyond this limit, it is suggested that the gold measuring electrode be removed from the cell and placed in a beaker of distilled water (200 ml) containing about two grams of sodium cyanide for about three minutes.

Calibration of Potential Cells The technique for the calibration at both potential levels is similar, and for each level in potential is as follows:

For the cyanide or reduced potential level, use a cyanide solution buffered to pH 8.4, made as follows: To 10 to 12 quarts of tap water* in a clean porcelain pail, add 100 g or 0.25 lb. sodium bicarbonate (NaHCO_3) and 2 g sodium cyanide (NaCN); then dissolve by stirring.

Drain sample pump and potential cell and recirculate this solution through cell assembly. Depending upon the recorder and chart range, it may be necessary to reverse the electrical connections at the cell in order to get this potential on scale. Record the potential until it becomes constant. This potential is the *calibrated cyanide potential* and should be so noted, due regard being made of any reversal of cell connections.

For the cyanate potential level, use a hydrogen peroxide test solution buffered to pH 8.4, since it has the same potential as cyanates. It is made as follows: To 10 to 12 quarts of tap water in a clean porcelain pail, add 100 g or 0.25 lb. sodium bicarbonate (NaHCO_3) and sufficient hydrogen peroxide to equal 2g H_2O_2 . Proceed as above, except that it will not be necessary to reverse cell leads. The recorded potential is the *calibrated cyanate or peroxide potential*.

*** If the tap water contains appreciable amounts of iron or manganese, it is advisable to calibrate the cells with test solutions made up with distilled water.**