

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WSG 72

Date Signed: March 7, 1994

MEMORANDUM

SUBJECT: Clarification on Chlorination BAT for Cyanide

FROM: William R. Diamond, Acting Director  
Drinking Water Standards Division, OGWDW

TO: Drinking Water Branch Chiefs, Region I-X

I am writing to inform you that one of the best available technologies (BATs) for cyanide is not defined specifically enough in the rule language for the Phase V regulation. Chlorine is listed as one of the three BATs for cyanide in §141.62(c) and §142.62(b). Chlorinating water containing cyanide at or above the MCL without any regard to pH can lead to a buildup of an equally toxic compound called cyanogen chloride. The proper terminology for this BAT is alkaline chlorination as was discussed in the preamble to both the proposed and final Phase V regulations. The rule language in §141.62(c) and §142.62(b) will be amended to state that the BAT is alkaline chlorination (pH  $\geq$  8.5) in the Phase VIb regulation.

In the meantime, please use the attached **Public Water System (PWS) Warning** developed by Region VIII when cyanide levels exceed the MCL and chlorination is selected as the BAT. The **PWS Warning** contains important information regarding: 1) the potential public health threat that can occur if chlorine is applied at too low of a pH; 2) reasons why alkaline chlorination is the BAT instead of just chlorination; 3) chemistry and minimum pH requirements of alkaline chlorination; and 4) guidelines on the application of alkaline chlorination.

Please forward this information to your State Drinking Water Program Directors as soon as possible so that they can share this information with public water systems when the MCL for cyanide is exceeded. EPA will be submitting this **PWS Warning** to the Journal of the American Water Works Association for their consideration for publication and more widespread distribution. If you have any questions about the **PWS Warning**, please call Jeff Kempic at (202) 260-9567, Bob Clement at (303) 293-1259 or Dr. Robert Benson at (303) 293-1694.

Attachments

cc: Robert J. Blanco, 4604  
Alan A. Stevens, TSD

## **PUBLIC WATER SYSTEM WARNING**

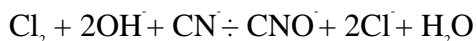
*APPLIES ONLY TO PWSs THAT USE CHLORINE TO OXIDIZE CYANIDE IN DRINKING WATER THAT EXCEEDS THE 0.2 MG/L MAXIMUM CONTAMINANT LEVEL (MCL).*

The Environmental Protection Agency (EPA) is publishing this warning to alert public water systems (PWSs) of the potential health hazard that results when chlorine ( $\text{Cl}_2$ ) is used to oxidize cyanide ( $\text{CN}^-$ ) in drinking water that exceeds the 0.2 mg/l MCL. When chlorine is used to oxidize water contaminated with cyanide, a disinfection by-product (DBP) called cyanogen chloride ( $\text{CNCl}$ ) is formed. EPA has no direct data on the toxicity of cyanogen chloride in drinking water. Due to this lack of toxicological data, EPA currently has no plans to regulate cyanogen chloride. However, **chronic exposure to cyanogen chloride may be as harmful as chronic exposure to cyanide at and above the MCL**. Additionally, cyanogen chloride is volatile and is extremely irritating to the respiratory tract at and above the MCL.

Chlorine quickly and effectively oxidizes cyanide and cyanogen chloride in a process called alkaline chlorination. Alkaline chlorination oxidizes cyanide to harmless bicarbonate ( $\text{HCO}_3^-$ ) and nitrogen gas ( $\text{N}_2$ ) by using excess chlorine at pH values greater than at least 8.5. The higher the pH the faster the reaction proceeds. Alkaline chlorination is prescribed over simple chlorination because of the need to destroy cyanide and cyanogen chloride as quickly as possible. EPA will change the regulations specifying the best available technology (BAT) for removing cyanide from chlorination to alkaline chlorination.

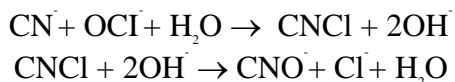
Because cyanogen chloride is not regulated and not routinely analyzed for, it is important that cyanogen chloride be oxidized at the water treatment plant prior to the first customer. Research on this subject has not been performed at levels representative of the MCL for drinking water. The available research has been conducted at low levels (less than 0.1 mg/l) and at high levels (10-50 mg/l) of cyanogen chloride. Research at both the high and low levels shows the same important observation: that the higher the pH, the faster the cyanogen chloride is oxidized to bicarbonate and nitrogen gas. Alkaline chlorination's ability to oxidize cyanide has made it a popular method to destroy cyanide and avoid the buildup of cyanogen chloride in the metal plating industry. This same technology can be used in the drinking water treatment industry to destroy cyanide when levels exceed the MCL. The process of alkaline chlorination proceeds through two oxidative steps.

The first-stage of alkaline chlorination converts cyanide to cyanate ( $\text{CNO}^-$ ). The following chemical equation can be used to calculate chemical dosages for chlorine and hydroxides in the first-stage:




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However, the reaction is not that simple. The oxidation of cyanide to cyanate progresses through the intermediate compound cyanogen chloride according to the following reactions:



The oxidation of cyanide to cyanogen chloride occurs instantaneously at all pH values. The oxidation of cyanogen chloride to cyanate occurs rapidly at pH values of 8.5 and above. The hypochlorite ion ( $\text{OCl}^-$ ) is the active chlorine species in the first stage. Research shows that within one hour the cyanogen chloride concentration has been significantly reduced<sup>1,2,3,4</sup>. Research conducted at the higher levels of cyanogen chloride show that at pH values less than 7.1 oxidation proceeds very slowly<sup>1,2</sup> (Figure 1 & 2). Research conducted at the lower levels of cyanogen chloride show that oxidation occurs at this very slow rate at pH 5.8<sup>3</sup> (Figure 3). Therefore, to avoid a buildup of cyanogen chloride, the first-stage of alkaline chlorination should be conducted at pH 8.5 or above. This is accomplished by the addition of hydroxide ions to increase the pH.

Lower temperature waters appear to slow the reaction down. Temperatures less than 20 degrees Celsius increase the reaction time<sup>4</sup> for the hydrolysis of cyanogen chloride (Figure 4). Therefore, even higher pH values or longer contact times may be necessary to compensate for slower reaction times in low temperature waters.

The second-stage of alkaline chlorination converts cyanate to bicarbonate and nitrogen gas and proceeds rapidly in the presence of excess chlorine. The following chemical equation can be used to

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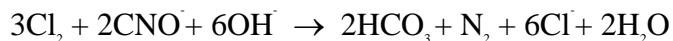
<sup>1</sup> N. S. Chamberlin and H. B. Snyder, Jr., Technology of Treating Plating Wastes, 1955, p. 277

<sup>2</sup> G. E. Eden et al., Destruction of Cyanide in Waste Water by Chlorination, J. Soc. Chem. Ind., 69: 244-249, (August 1950).

<sup>3</sup> Yuefeng Xie and David A. Reckhow, Stability of Cyanogen Chloride in the Presence of Sulfite and Chlorine, AWWA Proceedings of 1992 WQTC, Toronto, November 15-19, 1993.

<sup>4</sup> G. E. Eden and A. B. Wheatland, Effect of Temperature and the Presence of Hypochlorite on the Rate of Hydrolysis of Cyanogen Chloride in Alkaline Solution, J. Soc. Chem. Ind., 69: 166-169, (June 1950).

calculate chemical dosages for chlorine and hydroxides in the second-stage:



Hypochlorous acid (HOCl) is the active chlorine species that destroys cyanate. Even a small percentage of hypochlorous acid will oxidize cyanate. For example, at pH 8.5 (about 10% hypochlorous acid), cyanate is almost completely oxidized in 10 minutes (Figure 5). Oxidation occurs even more quickly at lower pH values.

In conclusion, the speed at which cyanogen chloride is oxidized is controlled by the concentration of the hypochlorite ion. The hypochlorite ion concentration increases as the pH increases and the entire reaction is dependent upon excess chlorine being available. The best way to know if the cyanogen chloride is oxidized below the MCL for cyanide is laboratory testing. However, EPA does not require this testing for the following reasons: 1) Labs available to perform this testing are few; 2) There is not a laboratory certification process for cyanogen chloride; 3) The holding times are very short making it difficult to assess the accuracy of the levels of cyanogen chloride in drinking water. Therefore, in lieu of testing, the following guidelines are provided to ensure that cyanide is completely oxidized to bicarbonate and nitrogen gas without the buildup of cyanogen chloride and that the water will be safe to drink prior to the first customer:

1. Maintain a pH of 8.5 or greater.
2. Maintain high free chlorine residual, but not greater than 4.0 mg/l.
3. Choose the percent removal needed and ensure that the contaminated water remains in contact with excess free chlorine, prior to the first customer, according to the following Table [adapted from the kinetics reactions developed by research conducted by Dr. David A. Reckhow and Yuefeng Xie, University of Massachusetts, Amherst].

Percent Removal	Ct (min-mg/l)
90	68
95	89
99	136
99.9	204

4. Compensate for the temperature effects with longer contact time or higher pH values.

EPA expects that the number of PWSs with cyanide greater than the MCL in their raw water to be low; however, those that do may have significant levels. For example, contamination from one

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EPA PWS cyanide warning

EPA contacts: Robert W. Benson (303-293-1694), Robert T. Clement (303-293-1259), Jeffrey B. Kempic (202-260-9567)

cyanide heap leaching operation has reported cyanide levels as high as 2.7 mg/l in the receiving stream. PWSs with very high levels of cyanide in their raw water should consult with the state and experts in this field to ensure that above guidelines are adequate.

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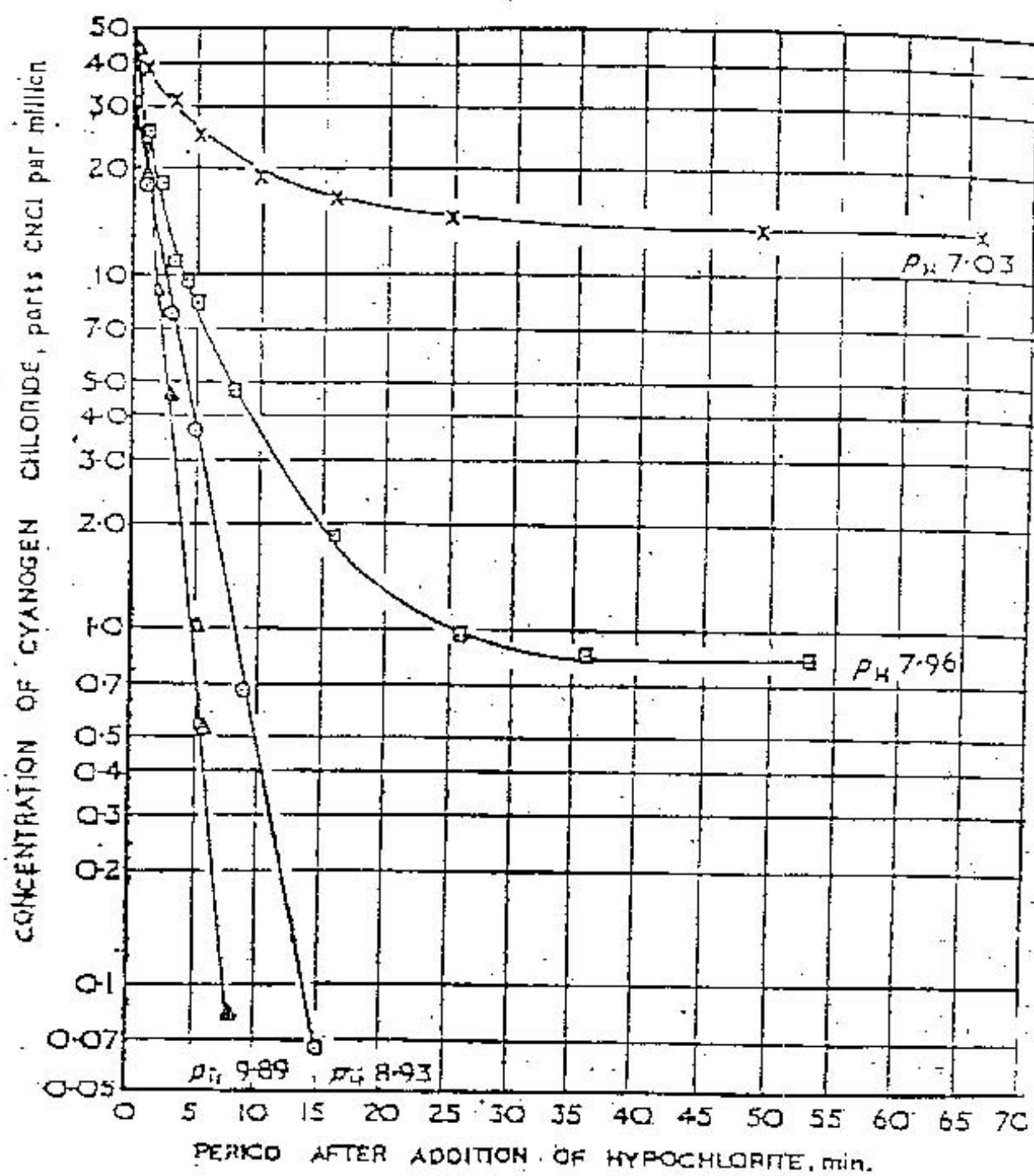


FIGURE 1 Removal of cyanogen chloride by the action of hypochlorite in buffer solutions at 20° C.<sup>2</sup>

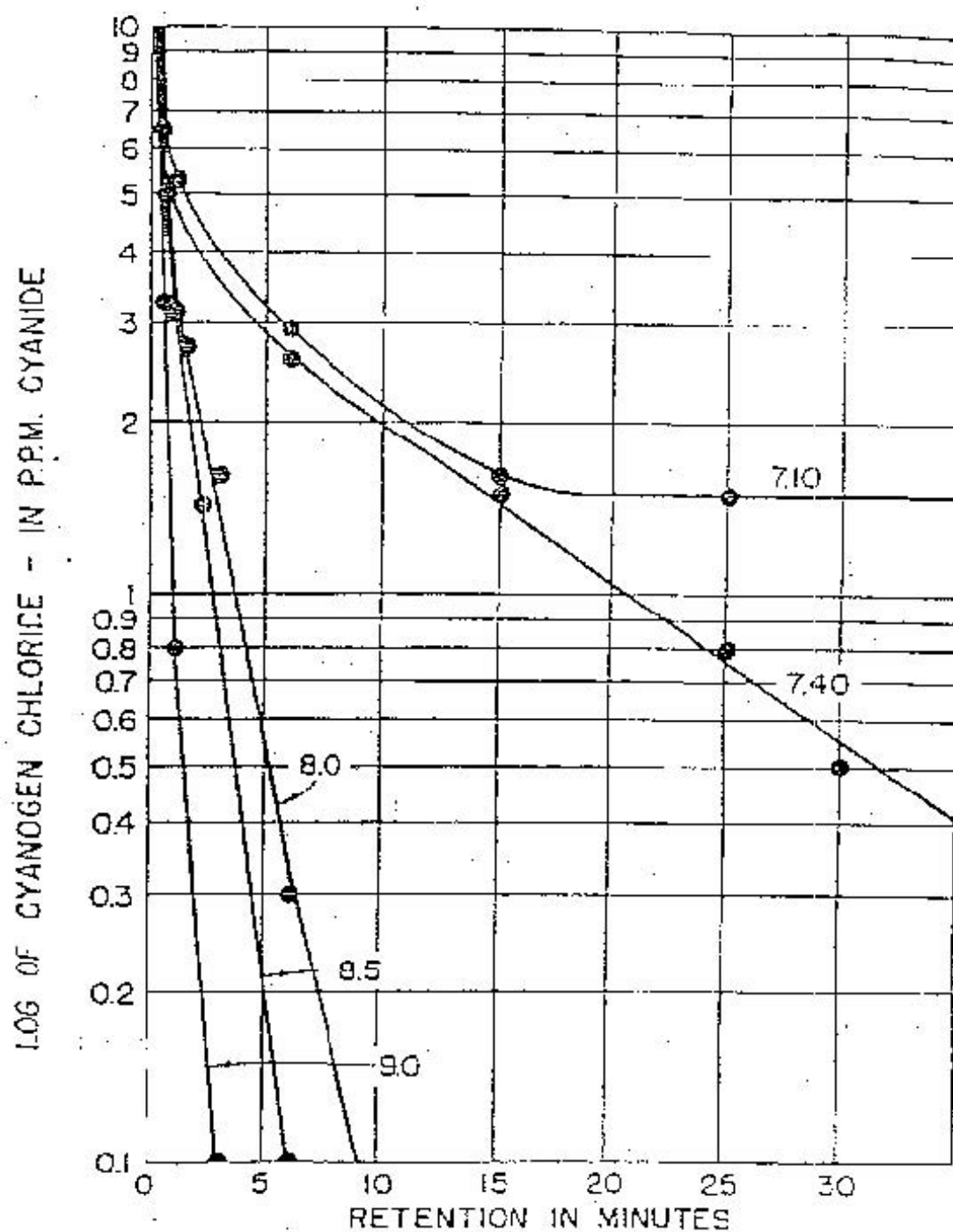
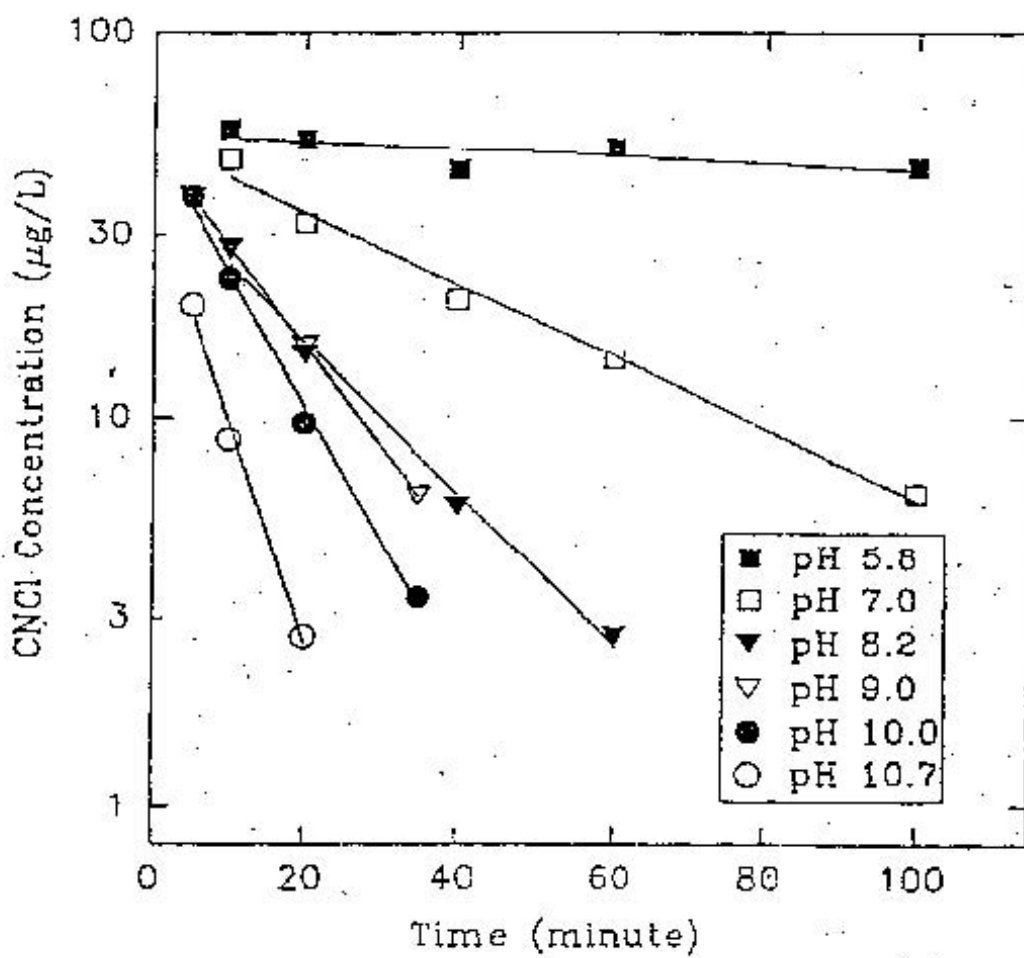
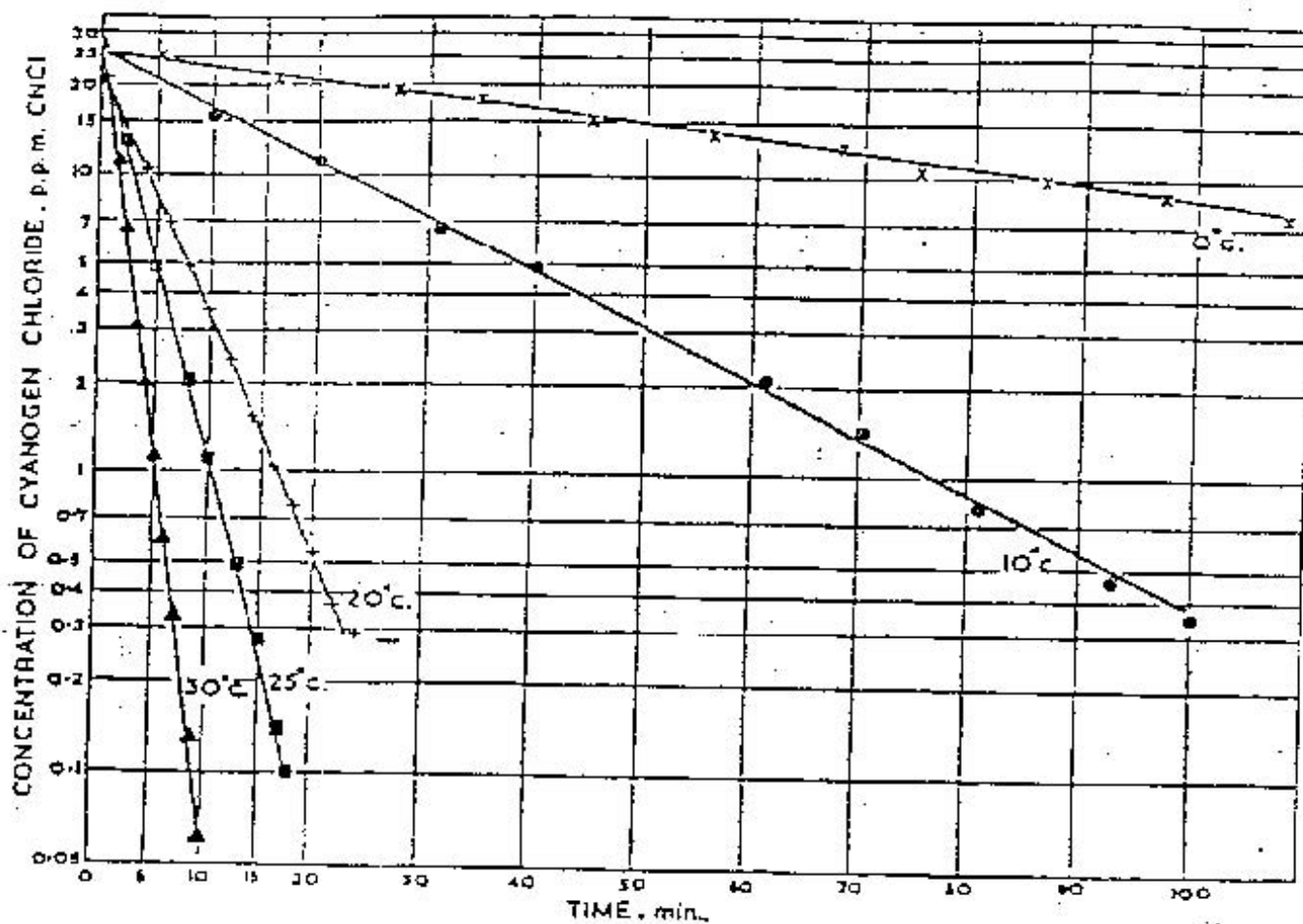


FIGURE 2 Effect of pH on hydrolysis of cyanogen chloride to cyanates in presence of a chloramine residual.<sup>1</sup>



**FIGURE 3**      **Degradation of CNCl in the Presence of Chlorine**  
**(1 mg/L)<sup>3</sup>**





**FIGURE 4** Effect of temperature on the rate of hydrolysis of cyanogen chloride at a pH value of approximately 11.4

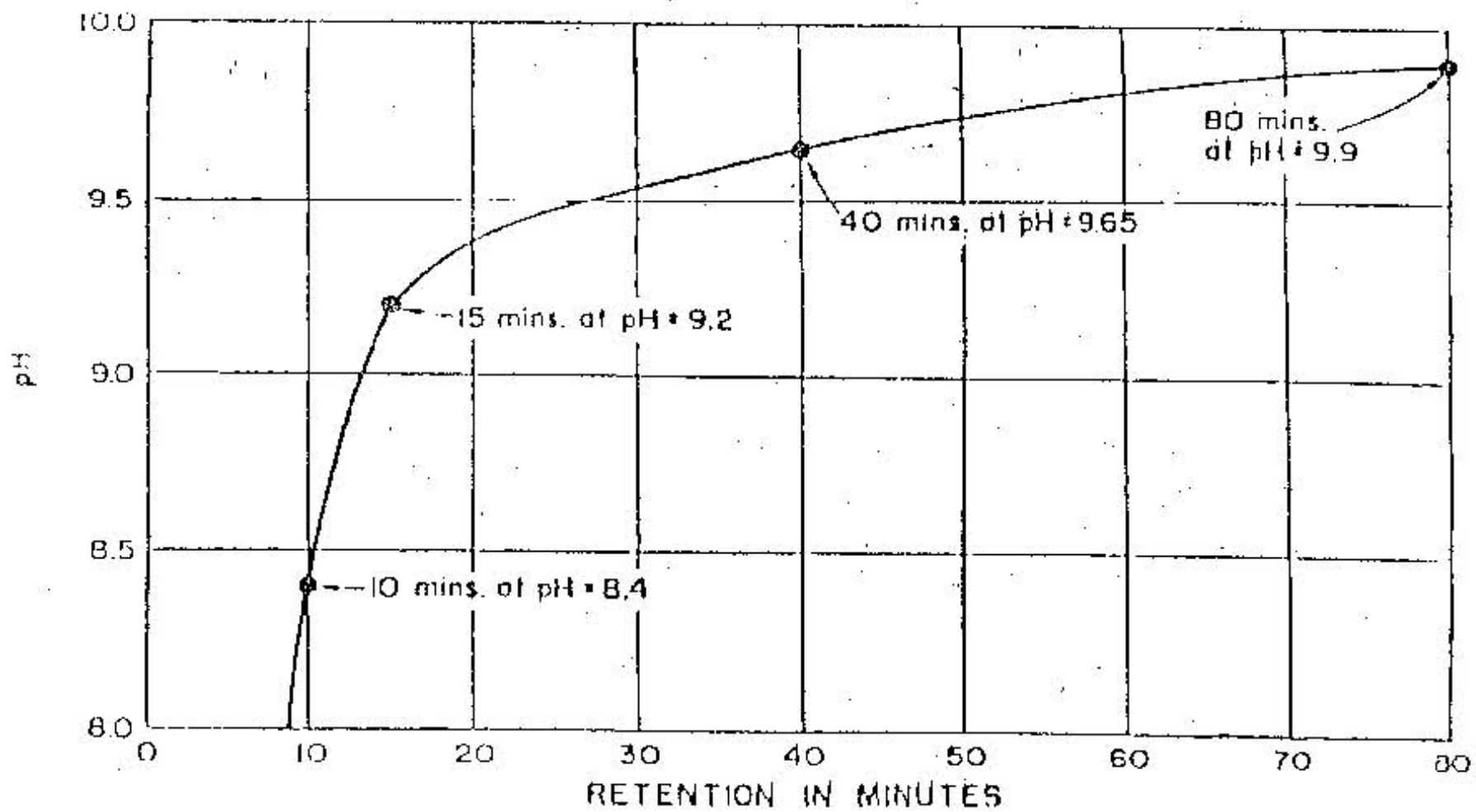


FIGURE 5 Time required for cyanate destruction.<sup>1</sup>

