

Study on destruction of cyanide treated with oxidized decontaminants

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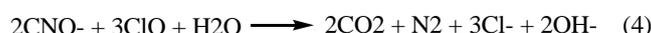
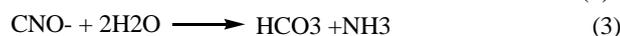
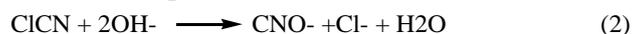
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Abstract. In this paper, hypochlorites and peroxides worked as decontaminants for destruction of cyanide ion. Main factors influencing the residual CN⁻ concentration after decontamination were investigated. And the amount of gasificated HCN and ClCN formed during the decontamination were measured, and their assessments on their damage were further discussed. Results indicated that degradation rate of KCN and gaseous by-products was closely related to the type of decontaminants, their concentration of active ingredients, KCN concentration, pH value and temperature *etc.* Generally, hypochlorites decontaminants reacted with cyanide ion more quickly than peroxides. When the amount of hypochlorite decontaminant was high above 2 times of its stoichiometric amount, the residual CN⁻ concentration could be down to 0.5 mg/L after 5 minutes, while for peroxides, it would take much longer for complete destruction. However, the massive gasificated ClCN produced intensely with hypochlorites decontaminant would cause relatively larger damage depth than that of HCN with peroxides.

1. Introduction

Simple cyanide salts (NaCN, KCN, etc.) are industrially made in large quantities and used in electroplating, metallurgy, electroplating, plastics, mining and organic synthesis *etc.* However, they are the most toxic and most likely to be in the environment^[1]. There are many international, national and local regulations and guidelines regarding cyanide in air, water and other media^[2]. As an example, the maximum contaminant level for cyanide set by the US EPA in drinking water is 0.2 mg/L^[3], while the European Union^[4] and China^[5], have an even lower limit of 0.05mg/L. And the maximum concentration being allowed discharged from industrial wastewater waters is 0.5 mg/L in China^[5].

The industrial methods for treating cyanide wastewater mainly include Alkali chlorine oxidation, SO₂-Air oxidation, electro-chemical method, complex precipitation method, acid recovery method, biological degradation and natural purification, *etc.*^[5-10]. Alkali chlorine oxidation method is often used to dispose of KCN leakage and other unexpected events^[5-10], commonly, hypochlorite is used. Process of decontamination reaction consists of three steps: the first reaction (formula (1)) is very fast, forming ClCN, if the value of pH keeps at 10.5~11.0; then, ClCN can be converted to CNO⁻ rapidly under a condition of pH>10; CNO⁻ is further hydrolyzed to inorganic salts(formula (3)), or carbon dioxide and nitrogen (formula (4)) if active chlorine is excessive^[4-8].



Due to its strong corrosivity and massive toxic by-product ClCN, the use of hypochlorites has been limited. Researchers around the world are working to explore a new environmentally friendly decontaminant. The peroxide decontaminant has received more and more attention, especially the organic peroxy acid decontaminant. A binary solid peroxy acid was developed in our lab. It is based on the reaction between the solid inorganic per-salt (A) and solid activator (B) after dissolved in the water to produce organic peroxide acid to achieve the purpose of decontamination^[11]. It has been proved high efficiency for degradation of CWAs with low corrosion. However, its application for destruction of cyanide is not studied deeply.

According to the mechanism of oxidation destruction reaction, the liquid residue after decontamination is affected by such factors, mainly including concentration of CN^- and active ingredients, pH value and environment temperature, *etc.* These factors also affect the production of ClCN/HCN which would form poisoned atmosphere, resulting damage to people without protection.

In this paper, three kinds of oxidizing decontaminant are adopted: hypochlorite, binary solid peroxide acid and hydrogen peroxide. They are used for decontaminating KCN solutions to investigate the influence of types of decontaminants and their dosage, KCN concentration, pH value and environment temperature on degradation of cyanide, and the formation and damage of gasificated ClCN/HCN were also studied.

2. Experimental

2.1. Apparatus

The residual cyanide ion concentration were detected by a cyanide ion selective meter (ISM) named HI 96714, bought from Italian Hanna Corporation. A detect tube (sensitivity: 1mg/L) were utilized for qualitative detection of gasificated ClCN and HCN. A HI2221 Specialty Laboratory pH/ORP/T Tester purchased from Italian Hanna Corporation was used for indication the change of temperature and pH online. The temperature was controlled by 501A Ultrathermostat purchased from Shanghai Experiment Instrument Factory.

2.2. Chemicals and Solution

KCN was purchased from International Chemical Import & Export Trade Co.,Ltd(China), and it was diluted to certain concentration (1.0% and 10.0%, wt %) before destruction reaction.

Decontaminants: Hypochlorite (Active Chlorine, AC>60.0%) and Binary solid peroxy acid decontaminant (A and B contained) obtained from Institute of Chemical Defense (China). They were both diluted to two kinds of different solution as decontaminants, that is 7.0 % or 2.0 % hypochlorite solution, A : B : H_2O = 1.0:1.0:10.0 or A : B : H_2O =1.0:0.5:10.0, respectively. 30 % (wt %) H_2O_2 purchased from Beijing Chemical plant was diluted to 10.0% (wt%) as another peroxide decontaminant.

End stopper: Na_2SO_3 (A.R.) was purchased from Tianjin institute of fine chemicals retrocession.

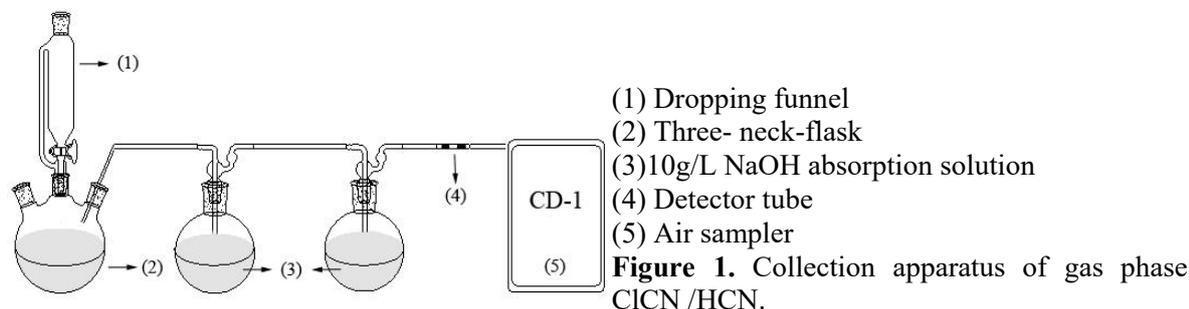
Analysis agents: KI (A.R.) was purchased from Xilong Chemical Co.,Ltd. Amylogen (A.R.) was purchased from Tianjin Fuchen Chemical Reagent Factory.

2.3. Pretreatment for analysis of residual concentration of CN^-

Residual concentration of CN^- was determined by HI96714. Before measurement, excess residual oxidant was reduced by Na_2SO_3 solution (12.6g/L), whose amount was determined in advance through a starch iodine titration method^[12].

2.4. Collection and analysis of gasificated HCN and ClCN

Absorption apparatus as the figure 1 shows. The gas phase product HCN was took in NaOH solution (10g/L) through two stage collection, while ClCN gas was absorbed by distilled cold water with five flasks. To ensure gas is completely collected, a detector tube was used for indication.



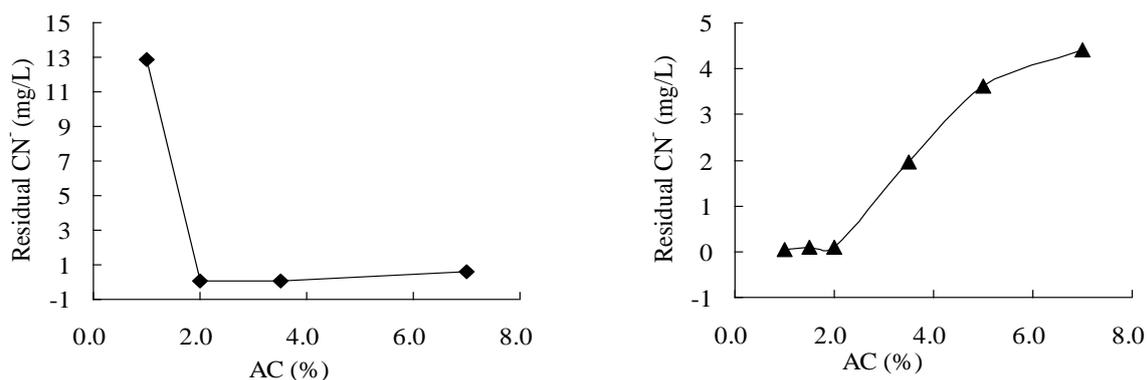
3. Results and Discussion

3.1. Destruction of cyanide ion by hypochlorite

3.1.1. Effect of Active chlorine concentration. Experiments were carried out under two kinds of conditions to investigate the effect of AC on destruction rate. First, the volume ratio of 1.0 % KCN and clear hypochlorite solution was fixed at 1.1:1.0 with active chlorine changing from 1.0 % to 7.0 %. The other was that the molar ratio of 1.0 % KCN and clear hypochlorite solution was fixed at 2.0:1.0, the volume of decontaminant decreased accordingly with increase of AC concentration. Results show in figure.2(a) and figure.2 (b) respectively.

Figure.2 (a) shows that AC played an important role in the destruction of KCN. 1.0% AC was not enough for complete degradation. The residual CN^- was about 12.9 mg/L after 5.0 minutes with the AC run out. And with AC value increasing to 2.0%, the residual CN^- was sharply down to 0.1 mg/L. However, when the AC value was further improved, promotion for destruction was not obvious, oppositely, excessive AC value resulted in higher residual concentration of CN^- , that is because AC decomposed too fast due to high temperature caused by intense reaction (Table 1).

Similar result was found in experiment under the other condition. Figure.2(b) shows relatively low AC value (below or at 2.0%) was favorable for complete decontamination. The residual CN^- concentration increased when AC value raise to above 2.0%.



(a) V(decontaminant):V(KCN)=1.1:1.0.

(1.0 % KCN: 50.0 mL, hypochlorite solution: 54.6 mL, reaction time: 5.0 min, $20 \pm 1^\circ\text{C}$)

(b) M(decontaminant):M(KCN)=2.0:1.0.

(1.0 % KCN: 50.0 mL, reaction time: 5.0 min, $20 \pm 1^\circ\text{C}$)

Figure 2. The influence of available chlorine concentration of hypochlorite for residual concentration of CN^- .

Table 1. Temperature, pH value and AC change with different hypochlorite solution

AC(%)	Highest temperature (°C)	pH value		AC after reaction (%)
		Before reaction	After reaction	
1.0	27.5	11.7	6.2	0.02
1.5	30.3		6.1	0.02
2.0	30.9		6.3	0.02
3.5	34.3		6.1	0.02
5.0	34.5		6.1	0.02
7.0	34.8		6.2	0.02

*: 1.0% KCN: 50.0 mL, M (decontaminant): M (KCN) = 2.0:1.0, reaction time: 5.0 min, environment temperature: $20 \pm 1^\circ\text{C}$

3.1.2. *Effect of pH.* Table 2 shows that pH had remarkable effect on the reaction, especially on highest temperature, AC concentration after reaction and production of ClCN gas. A strong alkaline kept in suspension of calcium hypochlorite and 84 solution, therefore, the reaction was relatively mild with AC remained more and obviously less production of ClCN. So maintaining a high pH was necessary through the destruction process.

Table 2. Influence of pH on the destruction reaction

Decontaminant	State	Highest T (°C)	pH value		AC(%)		Residual CN^- (mg/L)	ClCN gas
			Before reaction	After reaction	Before reaction	After reaction		
calcium hypochlorite	clear	30.9	11.7	6.3	2.0	0.02	0.09	++++
84 solution	suspension	25.3	12.1	12.1	2.0	0.3	0.03	+
	clear	25.0	11.4	11.7	2.0	0.4	0.01	+

*: 1.0 % KCN 50.0 mL, Decontamination of 2.0 % AC 54.6 mL, reaction time: 5.0 min, environment temperature: $20 \pm 1^\circ\text{C}$, ClCN gas was indicated by detector tube.

3.1.3. *Effect of concentration of KCN solution.* In the experiment, molar ratio of decontaminant to KCN was fixed to 2.0:1.0 and suspension of calcium hypochlorite was used as decontaminant. Result in Table 3 shows that concentration of KCN solution also has effect on the violence of reaction. Compared with 1.0 % KCN, the reaction between 10.0 % KCN and suspension of calcium hypochlorite was more fierce with much higher temperature.

In a word, hypochlorite can quickly destruct CN^- . Relatively low AC value, strong alkalinity and low concentration of KCN are favorable for safe and complete destruction of cyanide ion.

Table 3. Influence of KCN concentration on the decontaminating effect

KCN concentration	AC (%)	Highest Temperature in reaction (°C)	Residual liquid phase CN^- (mg/L)
10.0 %	2.0	43.4	0.01
1.0 %	2.0	25.3	0.03
10.0 %	7.0	89.8	ND
1.0 %	7.0	34.8	0.05

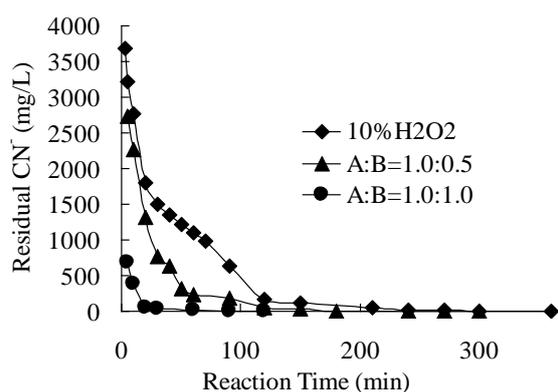
*: suspension of calcium hypochlorite; reaction time: 5.0 min, environment temperature: $20 \pm 1^\circ\text{C}$; ND: not be detected.

3.2. Destruction of cyanide by peroxide

3.2.1. *Different ratio of A to B.* Two decontaminants with different ratio of A to B (1.0:1.0, or 1.0:0.5) were introduced to react with 1% KCN. Although the same amount of active oxygen contented, the type

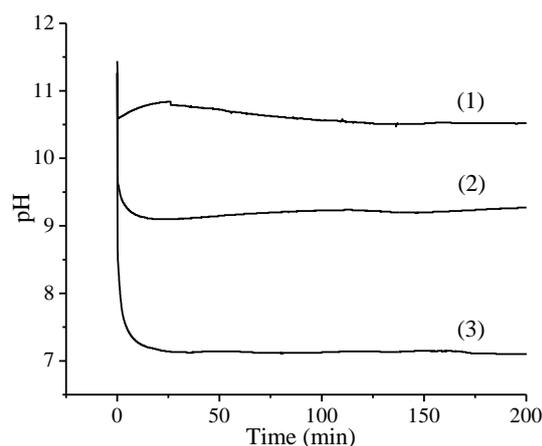
of active components, OOH^- or CH_3COOO^- are quite different. The amount of CH_3COOO^- was increased with the increase of the dosage of activator B (see in Table 4), resulting in a relatively strong oxidation. Figure.3 shows that the decontamination speed of solid peroxy acid with a ratio of 1.0:1.0 is greater than that of 1.0:0.5 as well as 10% H_2O_2 .

Figure.4 shows that pH is lower when the ratio of A to B is 1.0: 1.0, thus the oxidation ability of the decontaminant is stronger, and its degradation of KCN was also much faster. Therefore, pH may be another factor which affect the decontaminating rate.



(1.0% KCN 50.0 mL; solid peroxy acid decontaminant 19.0 mL; environment temperature 20 ± 1 °C)

Figure 3. Residual CN^- changed with reaction time under different ratio of A to B.



(1) 10.0% H_2O_2 ; (2) A:B=1.0:0.5; (3) A:B=1.0:1.0

Figure 4. pH value changed during reaction in these three decontaminants.

Table 4. Concent comparison of CH_3COOO^- in two kinds of peroxy acid

A:B:H ₂ O(w/w/w)	Molar ratio	Concent of CH_3COOO^-	
		Weigh (g)	Concentration (g/L)
1.0:0.5:10.0	2.0:1.0	0.35	5.0
	3.0:1.0	0.52	6.6
1.0:1.0:10.0	2.0:1.0	0.44	6.6
	3.0:1.0	0.67	8.8

3.2.2. Dosage of decontaminants. For different proportion of solid peroxy acid, the effect of molar ratio on decontaminating effect was not same. Figure.5 shows reaction become faster with the increase of the dosage of decontaminant when the proportion of A to B was 1.0:0.5. The time of decontaminating CN^- to industrial emission standards reduced from 4.0 h to 2.0 h. That is because the amount of CH_3COOO^- increases with the molar ratio becoming larger. However, when the proportion of A to B raised to 1.0:1.0, it has little effect on the decontamination rate. The reason may be the amount of CH_3COOO^- is large enough, either the molar ratio of A to B is 2.0:1.0 or 3.0:1.0.

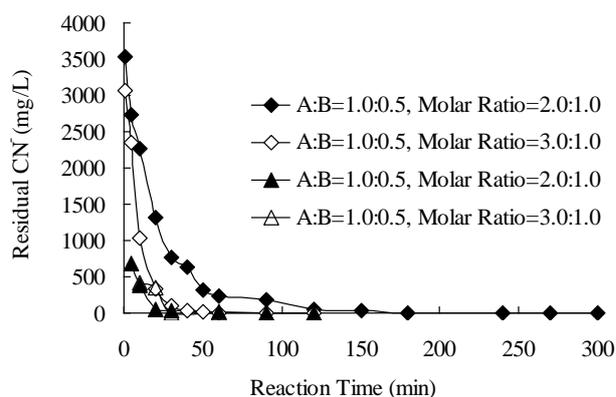


Figure 5. The change law of residual CN^- with time of different molar ratio. (1.0 % KCN 50.0 mL; environment temperature $20 \pm 1^\circ\text{C}$)

3.2.3. *Concentration of KCN solution.* KCN concentration was another main factor for the rate of decontamination. As table 5 shows, when the concentration of KCN solution is 10.0%, the decontamination rate is faster than that of 1.0 % KCN, and the temperature was up to 37.5°C while another was 24.1°C . Decontaminating 10.0 % KCN to emission standard required about 30 minutes, 8 times as much as that of 1.0 % KCN. In addition to the concentration, another possible reason may be temperature, reaction temperature of 10.0 % KCN is higher and more CN^- was converted to gas phase HCN.

Table 5. The change law of residual CN^- with time of different CN^- concentration

KCN concentration (%)	Decontamination time(min)	Highest reaction T ($^\circ\text{C}$)	Residual CN^-	
			C_{CN^-} (mg/L)	Residual rate(%)
1.0	10.0	24.1	2268.0	78.2
	30.0		775.0	26.7
	60.0		230.3	7.9
	120.0		42.9	1.4
	240.0		0.5	0.02
10.0	10.0	37.5	8.0	0.4
	30.0		0.02	0.002

(*: ratio of decontaminant: 1.0:0.5:10.0; molar ratio: 2.0:1.0; $20 \pm 1^\circ\text{C}$)

3.2.4. *Temperature.* Figure.6 shows the reaction rate of liquid phase is greatly influenced by the environment temperature. When the temperature rised up to 20°C , the time of decontaminating 10.0% KCN to discharge standards dropped. The higher the temperature, the faster the react, and the actual maximum temperature of decontamination reaction was 37.5°C while the environment temperature was 20°C . However, when the temperature was further increased to more than 30°C , the rate of the decontamination significantly slowed down, that was because the decomposition of active oxygen further speeded up. And, when the temperature was increased to 40°C , the actual maximum reaction temperature have reached as high as 57.6°C , the speed reduction caused by active oxygen reduction can not be ignored. The time of decontaminating CN^- to discharge standard at this point need 60.0 minutes.

In a word, solid peroxy acid reacted with KCN more mildly compared with hypochlorite solution. Relatively high concentration of active oxygen and KCN, suitable temperature and pH value are favourable for the destruction.

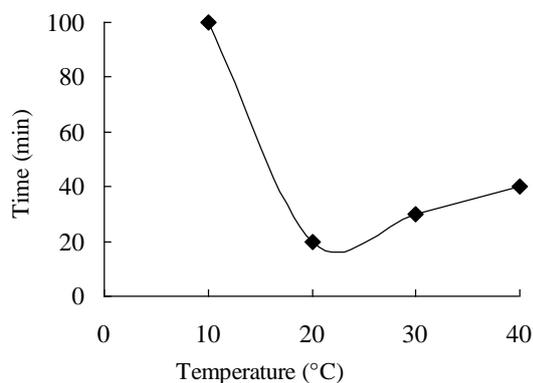


Figure 6. Reaction time reach 0.5mg/L under different environment temperatures. (10.0 % KCN; solid peroxy acid decontaminant(1.0: 0.5: 10.0) 38.0 mL)

3.3. Hazard assessment of HCN or C1CN

Generated gas phase was mainly C1CN when KCN was treated with hypochlorite solutions. The amount of C1CN produced from suspension was less than that from supernatant whether the active chlorine was 2.0 % or 7.0 % (Table 6), and the lower the concentration of AC, the less gas C1CN. When the active chlorine was 7.0 %, the formation rate of C1CN was as high as about 8.5 % and 9.9 % respectively.

Table 6. The amount of produced gases of C1CN and HCN during KCN decontamination^[13]

Decontaminants	V _{Decontaminants}	T (°C)	Reaction Time	Ratio of Total CN ⁻
None	0.0	10、 20		0.03%
		30	60.0 min	0.05%
		40		0.10%
		10	90.0 min	0.06%
Organic Peroxyl Acid (1.0:0.5:10.0)	38.0 ml	20	15.0 min	0.32%
		30	25.0 min	0.19%
		40	40.0 min	0.15%
		10		0.36%
Organic Peroxyl Acid (1.0:1.0:10.0)		20	5.0 min	0.48%
		30		0.90%
		40		3.30%
2.0 % Hypochlorite Solution (Suspension)	109.2 ml	20	5.0 min	0.26%
2.0 % Hypochlorite Solution (Clear)		20	1.0 min	>2.2%
7.0 % Hypochlorite Solution (Suspension)		20	1.0 min	8.49%
7.0 % Hypochlorite Solution (Clear)	31.2 ml	20	1.0 min	>9.89%

*: 10.0 % KCN solution: 10.0 mL.

The gas phase is mainly HCN when KCN is treated with peroxy acid. When the proportion of A to B was not same, the generation rate and amount of the HCN was affected by the temperature differently. The temperature affect little when the ratio is 1.0:0.5:10.0, the rate was similar to that of KCN hydrolyzed itself to HCN at different temperatures. However, when the ratio was 1.0:1.0, the formation rate of HCN was obviously larger and increased with temperature, about 3.3% of CN⁻ was translated into HCN per minute under the condition of 40°C. The damage depth caused by gas phase HCN with solid peroxy acid was less than C1CN generated with hypochlorite^[12]. And the damage depth is effected by amount of KCN, ratio of decontaminant, work speed, temperature and wind speed, etc. The more KCN, the smaller the wind speed, the greater the damage depth caused by HCN or C1CN.

4. Conclusions

In summary, when CN^- was treated with hypochlorite solution, the reaction was very intense, reaction temperature was high, residual liquid phase CN^- could reach discharge standard in few minutes; gas phase ClCN was produced instantly, forming poisoned air with high concentration and wide depth of damage, that may cause serious harm to people; and abundant insoluble solid wastes generated during the decontamination process need to be further disposed. While for peroxide decontaminant, the reaction was relatively mild, the decontamination speed and production rate of gas phase HCN could be deployed by changing the formula, however, the complete destruction time needed is longer, more than ten minutes; no insoluble solid waste formed after decontamination; the formation of gas phase HCN is relatively low. In addition, if chemical method was directly used after KCN leakage, no matter what kind of decontaminant, the dosage will be too large. To maximum recycle the KCN by physical method as far as possible first, then deal with it by decontaminants.

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