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Predicting the rate of hydrogen cyanide emission from surface water into the air: a critical review

Tổng quan về dự đoán tốc độ bay hơi của Hydrogen cyanide từ môi trường nước mặt vào không khí

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Abstract

Hydrogen cyanide (HCN) is a toxic chemical that is usually in the form of gas. Many kinds of industrial activities can result in the release of this toxin into surface water. This study relates to a mathematical tool, based in chemistry and physics, which can quickly and accurately predict the emission rate of HCN from surface water into the air. Such information on HCN emission rates is crucial in order for governments or other organizations to respond quickly and effectively to incidents of hazardous release of HCN, or to make scientifically sound decisions when planning projects that involve HCN. Specifically, this study examines the principle factors which affect the emission rate of HCN from surface water into the air. Then this paper presents and summarizes a series of equations that enable one to calculate the emission rate of HCN from surface water into the air. The study results show that the emission rate of HCN from surface water into the air can be calculated by applying a set of eight related equations.

Keywords: Hydrogen cyanide; volatilization.

Tóm tắt

Hydrogen cyanide (HCN) là một hóa chất độc hại thường tìm thấy ở dạng khí. Nhiều loại hình công nghiệp có thể thải chất độc này vào nước mặt. Vì vậy, việc có được một bộ công cụ toán học tính toán nhanh và chính xác tốc độ bay hơi của HCN từ môi trường nước mặt vào không khí là thực sự cần thiết. Dữ liệu về tốc độ bay hơi của HCN từ môi trường nước mặt vào môi trường không khí là dữ liệu quan trọng để chính quyền và các bên liên quan đưa ra các phản ứng một cách kịp thời và hiệu quả với các sự cố liên quan đến sự phát tán của HCN, hay phục vụ cho việc đưa ra các quyết định hợp lý trong việc lập kế hoạch cho các dự án liên quan đến HCN. Cụ thể, nghiên cứu này xem xét các yếu tố chính ảnh hưởng đến tốc độ phát thải của HCN từ nước mặt vào không khí. Sau đó, bài viết này trình bày và tóm tắt các phương trình tính tốc độ phát thải của HCN từ nước mặt vào không khí. Kết quả nghiên cứu cho thấy tốc độ phát thải HCN từ nước mặt vào không khí có thể được tính bằng cách áp dụng một bộ tám phương trình liên quan.

Từ khóa: Axit xianhidric; bay hơi.

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1. Introduction

Cyanide is commonly used to make or process many kinds of products, including plastics and other synthetics, precious metals, farm chemicals, coloring agents, nutritional supplements, chemicals to treat water, dyes and pigments, and numerous other chemicals and medicines [1]. Substantial amounts of cyanide are also involved in many industrial activities, such as the production of coal, iron, steel, and aluminum, as well as oil refinement. Some industrial processes, such as dyeing and gold mining, routinely produce and discharge hazardous waste water that includes toxins, such as hydrogen cyanide (HCN), which is a highly toxic gas.

When discharged as a liquid in a waste water solution, HCN will, under normal conditions, seek to volatize out of the solution and into the surrounding air. The location where waste water from gold mining operations is discharged and maintained is referred to as a tailings storage facility (TSF), and HCN volatilization from such facilities can easily contaminate the surrounding air [2, 3]. Of particular concern is that HCN gas is less dense than regular air, so once volatilized, it can rise quickly and disperse widely [4]. Previous studies have shown that volatilized HCN in this way reaches and threatens not only communities in the immediate vicinity, but potentially also areas many kilometers away from the site of release [3, 5, 6].

Both people and animals can unknowingly inhale HCN from a variety of sources [1, 2, 7-9]. Depending on concentration and duration of exposure, HCN can exert effects that are short term, long term, or even deadly [10]. HCN can reach and harm wildlife through inhalation, also through contaminated sources of food and water, after HCN contacts surfaces on the ground [11].

Prompt and effective response to hazardous incidents of HCN release requires a way to quickly analyze and understand how HCN volatizes and is dispersed through the air. Air Dispersion Modeling (ADM) provides an efficient solution to this need. ADM can quickly simulate not only the volatilization and dispersion of HCN from a release source into the air, but also the airborne chemical's eventual deposition down onto ground surfaces. Before giving ambient or surface concentration of HCN at any relevant location all of the time, ADM analyzes many input data that is including emission rate data.

The emission rate of HCN from a TSF of practical projects was often determined by field work and laboratory work, which was over a long period of time with complete equipment, and cost. To overcome these limitations, this study will give a calculation method of HCN emission from TSF into the air. The study's methods are based on reviewing and analyzing the published studies' results which related to the emission rate of HCN from solution into the air, and the exchange of gas from water to air.

2. Cyanide property

The term cyanide refers to any of several chemical compounds that include the **C≡N** group, which is referred to as the cyano group**.** The cyano group is made up of one carbon atom connected to one nitrogen atom with a triple bond. Common aqueous forms of cyanide can be divided into four major classes: free cyanide, metal–cyanide complexes, cyanate and thiocyanate species, and organocyanide compounds. Free cyanide comprises molecular HCN and cyanide anion.

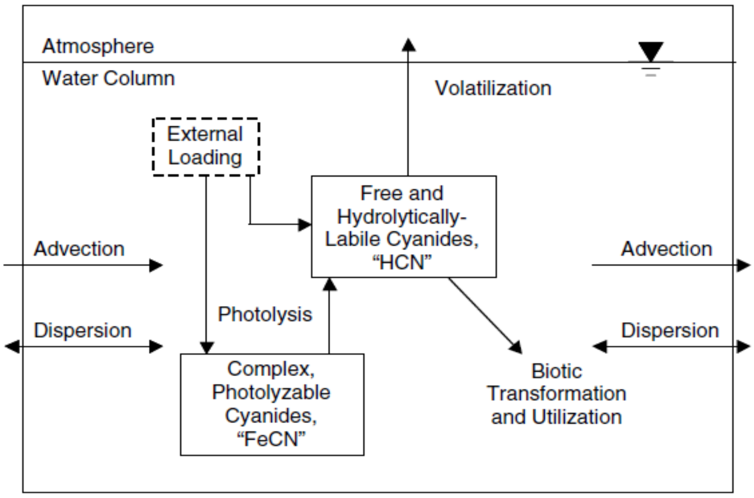

Figure 1. Sources of free cyanide, its transport, and its final fate in surface waters [1]

In water, cyanide compounds can transform to free cyanide. Figure 1 is a schematic illustration of the sources of free cyanide, its transport, and its final fate. The key processes to note are how hexacyanoferrate becomes transformed to free cyanide, how the cyanide becomes volatilized, and how some portion of the cyanide is transformed as it is utilized by microorganisms.

In water, free cyanide exists in two forms: hydrogen cyanide and cyanide ion (CN^-). The chemical formula for hydrogen cyanide is HCN, and the molecular weight is 27.03 g/mol [12]. HCN is a colorless gas or liquid, and it can volatile into the air, while CN^- never volatilizes [13]. The dissociation of free cyanide is according to the Reaction 1. Soluble hydrogen cyanide, HCN(aq), is a weak acid with a pKa of 9.24 at 25^0C [1]. When $pH < 9.2$, HCN is the dominant form of free cyanide. The proportion of free cyanide in the water volatile in the air depends on the pH level of solution, the lower pH, the higher percentage of free cyanide will volatize.

$$HCN \Leftrightarrow H^+ + CN^- \qquad (1)$$

3. Calculating the emission rate of HCN from water surface into the air

Numerous researchers have studied how various chemicals can volatilize from surface water into the air [14-18]. Conversely, chemicals in the air can also dissolve into surface water such as rivers, lakes, or seas. When the concentration of the chemical in the water (g/cm^3) and the concentration of the chemical in the air (also g/cm^3) are equal, this concentration is called the equilibrium constant (C_{equil}) for that chemical under current conditions. Whenever the two concentrations become unequal, the chemical will naturally migrate either from water to air or from air to water until the C_{equil} is restored [14].

To calculate the rate of HCN volatilization from water surface into the air, the theory on air-gas exchange was applied. According to Hemond and Fechner [14], the rate of the exchange of the chemical from a lake into the air depends on the thermodynamic and physical-chemical properties of the substance, such as its solubility, diffusivity, vapor pressure, and deviations from ideality. The exchange process can be described by the two-film theory of Liss [19], as shown in Figure 2 [14].

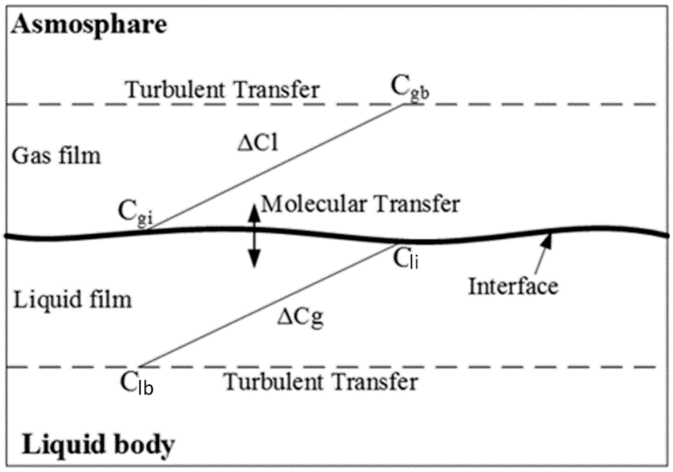

Figure 2. The two-film model for mass transfer from a water body to the atmosphere. C_{lb} and C_{gb} are the chemical concentration in the liquid bulk and gas bulk, respectively. C_{li} and C_{gi} are the equilibrium chemical concentration at the liquid interface in gas interface, respectively. ΔC_l and ΔC_g are the chemical concentration gradient in liquid and gas, respectively Liss [19]

Various studies have found that HCN volatilization from a liquid body follows first-order kinetics with respect to the concentration of aqueous HCN [20-22]. Assuming first-order kinetics, HCN volatilization can be expressed as follows:

$$-dC_{HCN}/dt = k_v \times C_{HCN}, \qquad \text{(Eq. 1)}$$

where dC_{HCN}/dt is the rate of volatilization (g/s×m^3), k_v is the volatilization rate constant (1/s), and C_{HCN} is the concentration of aqueous HCN (g/m^3).

The volatilization rate constant (k_v). Previous studies' reported values for k_v of HCN are summarized in Table 1. In addition, the k_v of *HCN* from the liquid film can be calculated according to the following equation [23]:

$$k_v = K_{OL,HCN}/Z, \qquad \text{(Eq. 2)}$$

where $K_{OL,HCN}$ is mass transfer coefficient of HCN (m/s); Z is the cyanide solution film thickness (m), which was calculated with the following equation [23]:

$$Z = D/K_{OL,HCN}, \qquad \text{(Eq. 3)}$$

where D is the molecular diffusion coefficient of HCN in water (m^2/s).

The molecular diffusion coefficient of HCN (D). The most significant physical parameter in the hydrogen cyanide transfer is the diffusion coefficient in both phases involved in the process (gas and liquid). In this context, the experimental data reported in the literature for the diffusion coefficient of HCN in air and water is limited. Klotz and Miller [24] found a diffusion coefficient ($D_{HCN\text{-}air}$) of 1.73×10^{-5} m^2/s, and Lotter [23] adapted the HCN diffusion coefficient in water ($D_{HCN\text{-}water}$) from Dodge and Zabban [25], obtaining a value of 1.72×10^{-9} cm^2/s at 20^{0}C.

HCN concentrations. The concentration of HCN that crossed the liquid film depends on many factors, such as the concentration of free cyanide and the pH of the solution. Notably, the thickness of cyanide solution which is sufficient for the exchange of gas to occur from water to air is 0.02 cm higher [14].

The mass transfer coefficient of a chemical ($K_{OL,HCN}$). Previous studies' values for $K_{OL,HCN}$ of HCN are summarized in Table 1. Most of the values for $K_{OL,HCN}$ in **Error! Reference source not found.**1 were produced by experimental activities, while some others were extrapolated from experimental data. In general, the values of $K_{OL,HCN}$ from the various sources are not too different with the mean value being 7.5×10^{-6} (m/s) and the standard deviation being 0.018. The mass transfer of HCN across an interface can be described by the finite difference approximation of Fick's first law of diffusion. This assumes that the chemical will move spontaneously from an area of higher concentration to an area of lower concentration to equalize any differences in concentration between the different layers in the mixture. Using this approach, the mass transfer coefficient of HCN is calculated using the following equation [23]:

$$1/K_{OL,\,HCN} = 1/K_{l,HCN} + RT/H_{HCN}\times K_{g,HCN}, \qquad \text{(Eq. 4)}$$

where $K_{l,HCN}$ is the liquid phase mass transfer coefficient (m/s), R is the universal gas constant (atm×m^3/(molxK), T is the absolute temperature (K), $K_{g,HCN}$ is the gas phase mass transfer coefficient (m/s), and H_{HCN} is Henry's law constant for equilibrium partitioning of HCN between the liquid and gas phases (pa×m^3)/mol).

Henry's law constant for equilibrium partitioning of HCN (H_{HCN}). Previous studies' values for H_{HCN} are summarized in Table 1. The most recent report found is from 2010, with the value 0.101 (atm×l/mol) [26]. Most of the values for H_{HCN} in **Error! Reference source not found.**1 were produced by experimental activities, while some others were extrapolated from experimental data. In general, the values of H_{HCN} from the various sources are not too different with the mean value being 13.45 (pa×m^3/mol).

Table 1. Summary of the values of Henry's Law constant for HCN

Temperature (°C)	H_{HCN} (pa×m^3/mol)	[CN$^-$] (ppmv)	Ionic stength	Method	Reference
25	11.65	100	0	Experimental	[25]
64	13.48	1950	0	Experimental	
85.5	33.74	49380	0	Experimental	
25	10.94	197000	Not given	Extrapolated	[27]
25	12.36 -	100	0	Experimental	[28]
	14.59		0	Calculated from experimental	[29]
30	8.51	265	0.75		
	9.22		3		
25	11.35	4.42	0	Experimental	[23]
	13.37		1		
	14.59 ± 3.95		3		
	17.53 ± 4.96		5		
20	22.39 ± 6.79	2-40	1	Experimental	[23]
25	8.31	21	5	Not given	[26]
25	13.37	318-376	0	Experimental	[26]
25	7.90	0.8-36	0.1	Equation	[26]
25	11.15			Experimental	

H_{HCN}: Henry's Law constant for HCN

[CN$^-$]: Cyanide concentration

Additionally, H_{HCN} can be estimated by using equations. Different empirical equations, which reported based on experimental data, have been used to study the dependence of temperature on the Henry's law constant Table 2.

Table 2. Empirical equations can be applied to calculate Henry's law constant

Empirical equations	Unit	Valid range	Note
Log H_{HCN} = -1272.9/T + 6.238	H_{HCN} (mmHg/M) T (K)	180-9,000 mg/l 20-95^{0}C	[30]
Ln H_{HCN} = -8205.7/T – 25.323	H_{HCN} (M/atm) T(K)	0.8-36 mg/l 14-38^{0}C	[26]
Ln H_{HCN} = -3638.8/T + 18.539	H_{HCN} (kPa/mol fraction) T(K)	0-35,000 mg/l 0-50^{0}C	[31]

This study suggests applying the empirical equation which was created by Estay, et al. [31] based on three reasons: it is the newest empirical equation on this term, this equation can be applied in a wide temperature, and HCN concentration range.

$$\text{Ln } H_{HCN} = -3638.8/T + 18.539 \qquad \text{(Eq. 5)}$$

where H_{HCN} is Henry's Law constant (kPa/mol and, *T:* Temperature (K).

The liquid phase mass transfer coefficient of hydrogen cyanide ($K_{l,HCN}$). Kavanaugh [32] pointed out that few researches measure and publish HCN's liquid- and gas-film mass transfer rates, so data are not readily available. However, it is possible and feasible to calculate the rates using correlation equations with mass transfer rates previously determined for other substances that are more common and more studied than HCN. For example, the mass transfer properties of oxygen have been the subject of numerous past studies, so oxygen can serve as a more understood reference for calculating the liquid-film mass transfer coefficients of other substances. This use of data from a more common substance with correlation equations has been applied to calculate HCN's liquid-film mass transfer coefficient. The current study uses the following equations to estimate the $K_{l,HCN}$ [33]:

$$K_{l,HCN} = K_{l,O}\times(32/M_{HCN})^{0.25}, \qquad \text{(Eq. 6)}$$

where M_{HCN} is the molecular weight of HCN (g/mol), and $K_{l,O}$ is the oxygen-transfer coefficient in the water phase (m/s) [1].

The gas phase mass transfer coefficient of hydrogen cyanide ($K_{g,HCN}$). In a similar way, it is also possible to calculate the $K_{g,HCN}$ using the rates of water vaporization into the air, as in the following equation:

$$K_{g,HCN} = K_{g,H2O}\times(18/M_{HCN})^{0.25}, \qquad \text{(Eq. 7)}$$

where $K_{g,H2O}$ is the water vapor transfer rate into the air (m/s) [33].

By combining Equations 2 and 4, the volatilization rate constant (k_v) of HCN from the liquid film was calculated as shown in Equation (8) below:

$$k_v = 1/Z\times(1/K_{l,HCN} + RT/(H_{HCN}\times K_{g,HCN})). \qquad \text{(Eq. 8)}$$

Finally, the emission rate for HCN is then calculated using Equation 1 and 8.

Conclusion

The emission rate of HCN from the surface of the water surface into the air can be predicted by applying a set of eight formulas created from this study. The value of some parameters can be acquired from available sources, while the value of the remaining parameters can be achieved by applying the formulas in this study to calculate.

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