Modeling of natural cyanide attenuation in tailings impoundments

M.M. Botz and T.I. Mudder

Abstract

Cyanidation tailings disposed of in a surface impoundment experience a loss of cyanide due to natural attenuation, which frequently reduces the cyanide concentration to very low levels. Quantifying cyanide losses in terms of impoundment geometry, local weather conditions and feed-solution chemistry has been largely empirical in spite of the fact that, in many cases, mining operations rely on surface impoundments to reduce cyanide to below an internally regulated concentration or below an effluent limitation. To permit a quantitative evaluation of cyanide losses in an impoundment, a computer simulation was developed to estimate the losses of free, weak acid dissociable (WAD) and total cyanide due to dissociation, photolysis and volatilization. Results of the model are compared with data collected for a North American tailings impoundment in 1998.

Key words: Cyanide, Cyanide attenuation, Tailings impoundments, Modeling and simulation

Introduction

A typical milling and cyanidation circuit utilizes a surface impoundment for permanent storage of tailings solids. As illustrated in Fig. 1, many factors influence the overall water and cyanide balance in an impoundment. Quantification of an impoundment water balance is largely statistical due to the influence of weather conditions. However, reasonable probability bounds can be placed on the water balance to allow development of a useful site water-management plan. Conversely, quantification of an impoundment cyanide balance is more difficult because of its dependence on the water balance, weather conditions, impoundment geometry and tailings chemistry, all of which may vary significantly over the life of a mine. Because of the complexity involved in completing an impoundment cyanide balance, such balances are frequently not conducted, even though cyanide losses in an impoundment directly influence site operating costs, such as those associated with sodium cyanide purchases or the operation of a cyanide detoxification plant. For planned mining operations, coupling tailings impoundment design with goals for minimizing or maximizing cyanide attenuation in an impoundment would facilitate development of a cyanide management plan. This would result in the development of more accurate site operating costs, would potentially simplify the impoundment closure and would address issues associated with impoundment toxicity during the permitting stage.

Generally, the volume of water contained in an impoundment increases with time as the tailings solids and their entrained liquid accumulate in the impoundment. However, in almost all cases, there is a net loss of cyanide from an impoundment — a result of natural cyanide attenuation. Overall, natural attenuation is a complex process that may include the following routes of cyanide losses from solution (Smith and Mudder, 1991):

- volatilization,
- chemical oxidation,
- biological oxidation,
- hydrolysis,
- precipitation,
- complexation and
- sorption.

These reactions may take place in the supernatant solution or in the tailings sediment. However, the predominant route of cyanide loss is typically ascribed to hydrogen cyanide volatilization from the impoundment water surface. Schmidt et al. (1981) found from tests carried out in Canada that volatilization of hydrogen cyanide accounted for 90% of the cyanide removed from solution in a tailings impoundment, while a combination of other reactions accounted for the remaining 10%.

It was discovered that the loss of hydrogen cyanide occurs according to a first-order rate equation (Simovic, 1984), which means that the rate of loss of hydrogen cyanide from an impoundment is directly proportional to the hydrogen cyanide concentration in solution. Mathematically this is represented by

$$\frac{d[\mathrm{HCN}]}{dt} = -K[\mathrm{HCN}] \qquad (1)$$

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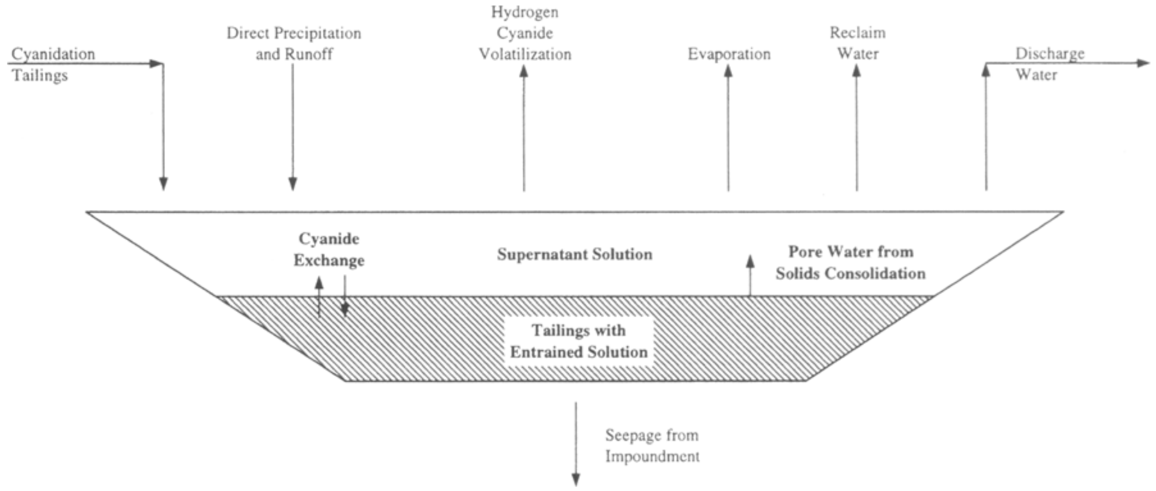


Figure 1 — Basic water and cyanide balance for a tailings impoundment.

where

[HCN] represents the molar concentration of aqueous hydrogen cyanide in the impoundment supernatant solution,

t is time and

K is the first-order rate constant.

For a tailings impoundment with a supernatant pond that is assumed to be completely mixed, the rate constant k is given by

$$k = \left(\frac{A}{V}\right) Kv \qquad (2)$$

where

A is the surface area of the supernatant pond exposed to the atmosphere,

V is the volume of solution in the completely mixed portion of the supernatant pond and

Kv is the first-order volatilization rate constant for hydrogen cyanide.

Substituting this into Eq. (1) yields:

$$\frac{d[\mathrm{HCN}]}{dt} = -\left(\frac{A}{V}\right) Kv[\mathrm{HCN}] \qquad (3)$$

The significance of the parameters in Eq. (3) are:

- The term A/V is the inverse of the average depth of the impoundment, commonly referenced as $1/Z$. Note that, as the surface area of the impoundment increases, the hydrogen cyanide volatilization rate increases. Similarly, as the volume of the impoundment water body increases, the hydrogen cyanide volatilization rate decreases. The term A/V is a physical property of a tailings impoundment and not a function of weather conditions or solution chemistry.
- The hydrogen cyanide volatilization rate constant Kv is influenced by factors that accelerate or slow the rate of hydrogen cyanide volatilization, including temperature, wind speed, turbulence on the water surface and the degree of mixing in the impoundment water body. This rate constant is dependent on local weather conditions, but it is not normally a function of the impoundment geometry or chemistry.

Table 1 — Common metal-cyanide complexes.

Free cyanides	Copper cyanides	Iron cyanides	Nickel cyanides	Zinc cyanides
HCN	$Cu(CN)_2^-$	$Fe(CN)_6^{-3}$	$NiCN^+$	$ZnCN^+$
CN-	$Cu(CN)_3^{-2}$	$Fe(CN)_6^{-4}$	$Ni(CN)_4^{-2}$	$Zn(CN)_2^0$
	$Cu(CN)_4^{-3}$		$Ni(CN)_5^{-3}$	$Zn(CN)_3^-$
				$Zn(CN)_4^{-2}$
				$Zn(CN)_5^{-3}$

- The product of Kv and A/V is the specific hydrogen cyanide volatilization rate constant and is a physical property of an impoundment. This constant changes with time as weather conditions vary or as the impoundment geometry changes, but it does not vary with changes in solution chemistry.

The terms A/V and Kv are a function of time according to changes in weather conditions and impoundment geometry variations. Therefore, an exact solution to Eq. (3) has not been provided. Rather, the solution to Eq. (3) is achieved by solving the equation for a discrete time step according to impoundment geometry, weather conditions and cyanide and metal concentrations appropriate for the time step. Repeating the solution for a large number of time steps yields the time-vs.-concentration solution to the equation.

Integral with the time-step calculations is the mathematical solution of cyanide equilibria relations required to determine the value of [HCN] used in Eq. (3). If there are no cyanide-complexing metals in the impoundment solution, calculation of [HCN] in Eq. (3) is straightforward. However, milling effluents typically contain copper, iron, nickel, zinc or other metals, which complicate the calculations.

Even a small concentration of a complexing metal affects the equilibrium concentration of hydrogen cyanide in solution, and in all cases complexing metals decrease the equilibrium hydrogen cyanide concentration and the overall rate of hydrogen cyanide volatilization. Note that, although complexing metals lower the overall rate of hydrogen cyanide volatilization, the volatilization rate constant does not change with the solution chemistry, as it is a physical property of an impoundment. The effect of the presence of complexing metals is to lower the value of [HCN] used in Eq. (3), thereby lowering the overall rate of hydrogen cyanide volatilization.

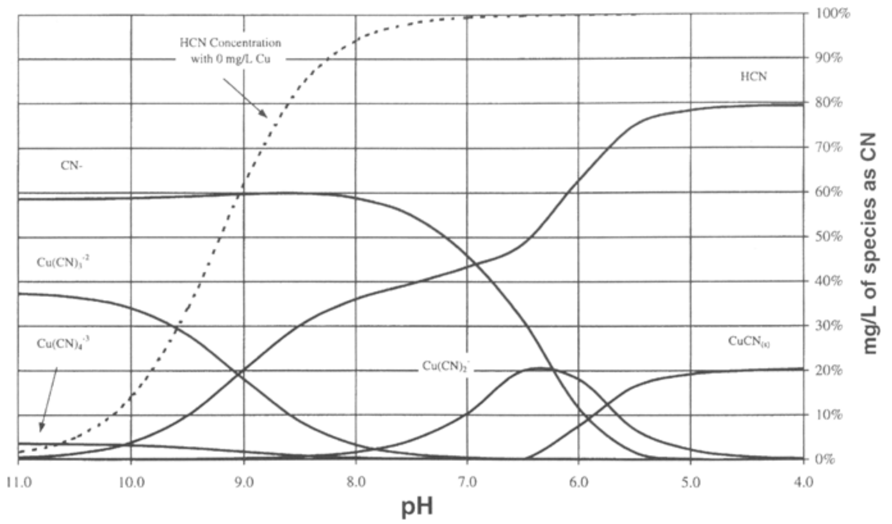
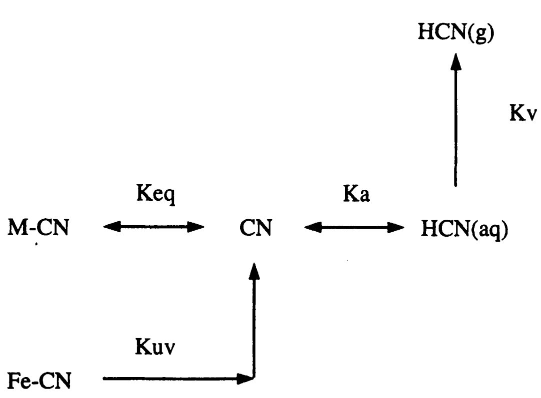


Figure 2 — Copper-cyanide species distribution vs. pH (100-mg/L cyanide and 50-g/L copper).



M = metal cation (including iron)

Keq = metal-cyanide equilibrium constant

Ka = HCN/CN acid dissociation constant

Kuv = photolysis rate constant

Kv = HCN volatilization rate constant

Figure 3 — Routes to hydrogen cyanide volatilization.

The effect of pH on the rate of hydrogen cyanide volatilization is similar in that a lower pH favors the formation of hydrogen cyanide and thus increases its rate of volatilization.

Table 1 lists the metal-cyanide complexes most commonly found in tailings impoundment solutions. Using copper as an example, Fig. 2 shows the equilibrium concentrations of the three soluble copper-cyanide species for the case of 100 mg/L total cyanide and 50 mg/L copper in solution at 25°C. As shown in Fig. 2, approximately 20% to 40% of the cyanide is present as hydrogen cyanide at a pH in the range of 7.0 to 9.0, which is a typical pH range observed in impoundment solutions. The influence of copper on the equilibrium hydrogen cyanide concentration is illustrated by the dashed line in Fig. 2, which shows the concentration of hydrogen cyanide that would be present if there were no copper in solution. With no copper present, approximately 60% to 100% of the cyanide would be present as hydrogen cyanide at a pH in the range of 7.0 to 9.0. This example illustrates the significant effect that complexing metals have on the equilibrium concentration of hydrogen cyanide.

As indicated in Table 1, iron forms two complexes with cyanide, with the Fe(III) complex being the predominant specie found in surface impoundments. Iron-cyanide complexes are very stable and dissociate only to a small degree under ambient conditions. However, these species are photolytically active and readily dissociate in the presence of ultraviolet (UV) radiation with a wavelength in the range of approximately 300 to 500 nm (Broderius and Smith, 1980). The rate of photolysis is primarily dependent upon UV intensity. However, pH, temperature and iron-cyanide concentration have been found to influence the photolysis rate (Broderius and Smith, 1980). Therefore, in addition to the equilibrium dissociation of iron cyanides, there is the irreversible dissociation of iron cyanides through photolysis, which occurs in impoundments exposed to UV. Iron-cyanide photolysis has been found to be first order, and the rate equation is written as:

$$\frac{d[\mathrm{Fe-CN}]}{dt} = -Kuv[\mathrm{Fe-CN}] \qquad (4)$$

where

[Fe-CN] is the molar concentration of the iron-cyanide species,
t is time and
Kuv is the photolysis rate constant.

The reaction mechanism for the photolytic decay of iron cyanides is not clearly understood. However, it has been observed that each mole of Fe(II) and Fe(III) cyanide dissociates to yield 5 and 3 moles of free cyanide, respectively, out of the 6 moles of cyanide bonded to the unreacted iron-cyanide species (Broderius and Smith, 1980). The fate of the remaining 1 and 3 moles of cyanide, respectively, are not presently known.

The photolysis rate constant for iron cyanides is time dependent because of seasonal and daily variations in UV intensity according to the position of the sun. As with Eq. (3), the solution to Eq. (4) is achieved by solving the differential equation in a series of time steps along with repetitive solution of metal-cyanide equilibria relations.

Model structure

The present approach parallels the presentation of Simovic (1984), Simovic et al. (1984) and Simovic and Snodgrass (1989) in that several reaction steps are included in calculating the rate of hydrogen cyanide volatilization. As shown in Fig. 3, it is assumed that metal-cyanide complexes, including iron-cyanide complexes, exist in equilibrium with the cyanide anion and metal cations according to values of individual equilibrium constants. At the same time, the cyanide anion exists in equilibrium with aqueous hydrogen cyanide, which volatilizes from solution according to a location and time-dependent volatilization rate constant. Contributing to the formation of the cyanide anion is the photolytic dissociation of iron cyanides according to the photolysis rate constant.

In the present work, it is assumed that metal cyanides exist in equilibrium, as indicated by the reversible reactions in Fig.

3. The validity of this assumption may be debatable, and a model developed by Simovic et al. (1984) was based on the premise that individual metal-cyanide species are not in equilibrium, rather they experience first-order decay with rate constants characteristic to each metal.

However, data collected by the authors, Broderius (1973) and Maracle (1992) suggest that, for reaction time periods on the order of weeks to months, the assumption of metal-cyanide equilibrium is appropriate. Functionally, each of the reaction steps illustrated in Fig. 3 are quantified as follows:

Metal-cyanide equilibria and cyanide–hydrogen cyanide equilibrium. Mathematical solution of metal-cyanide equilibria as a function of pH and temperature is achieved through numerical iteration according to equilibria constants for each metal-cyanide complex. Equilibria constants are calculated as a function of temperature according to data presented by Zemaitis et al. (1986) and Flynn and McGill (1995). Attendant with calculation of metal-cyanide equilibria is mathematical determination of the cyanide–hydrogen cyanide equilibrium, which gives the concentration of aqueous hydrogen cyanide used in Eq. (3). Typical results of this procedure are presented in Fig. 2 for a simple copper-cyanide system.

Iron-cyanide photolysis. Data presented by Zepp and Cline (1977) and Broderius and Smith (1980) is used in conjunction with GCSOLAR, a photolysis rate model developed by the US Environmental Protection Agency (1988), to calculate photolysis rate constants. Much of the input data required for the use of GCSOLAR with iron cyanides is provided by Broderius and Smith (1980), though physical and chemical properties of a specific impoundment are also required. Photolysis rate constants can be calculated by GCSOLAR as an average over the depth of a water body for each season of the year. The constants must be corrected for pH, temperature and iron-cyanide concentration according to data presented by Broderius and Smith (1980).

Hydrogen cyanide volatilization. Calculation of the hydrogen cyanide volatilization rate constant is substantially empirical, and several methods have been presented (Smith et al., 1980; Thomas, 1990; US Environmental Protection Agency, 1994; Sadek et al., 1996; Eastern Research Group, 1997). In addition, published values of hydrogen cyanide volatilization constants have a large range (Murphy and Robertson, 1979; Simovic, 1984; Simovic and Snodgrass, 1989). The approach in the current model is to calculate the volatilization rate constant according to the methods of Thomas (1990) and US Environmental Protection Agency (1994) to provide an approximate range of values for the rate constant. Time-vs.-cyanide concentration data are then generated for the range of hydrogen cyanide volatilization rate constants, and the results are assumed to bracket the solution. As variations in weather may be considered random and there is a degree of uncertainty in the hydrogen cyanide volatilization rate constant, the physical and chemical data for an impoundment and the site water balance, time-vs.-cyanide concentration results would be expected to represent a probabilistic solution rather than a exact solution.

The overall model calculation sequence is depicted in Fig. 4. Calculations are conducted for a series of discrete time steps in which metal-cyanide equilibria relations are solved, iron cyanides dissociate as a result of photolysis, and cyanide and metals are removed from solution through precipitation and volatilization reactions. The time step for the iterative calculations is usually on the order of 0.1 to 1.0 day, and it is assumed during this time step that equilibrium is established in solution and that photolysis and volatilization proceed according to an exponential decay function. Note that during the iterative procedure, constants for equilibria, photolysis, solubilities and volatilization are recalculated according to the time-dependent values of metals and cyanide concentrations, pH, temperature, UV intensity, weather conditions and impoundment geometry. Results from each iteration step are used in conjunction with the impoundment water balance to calculate metals and cyanide concentrations as a function of time.

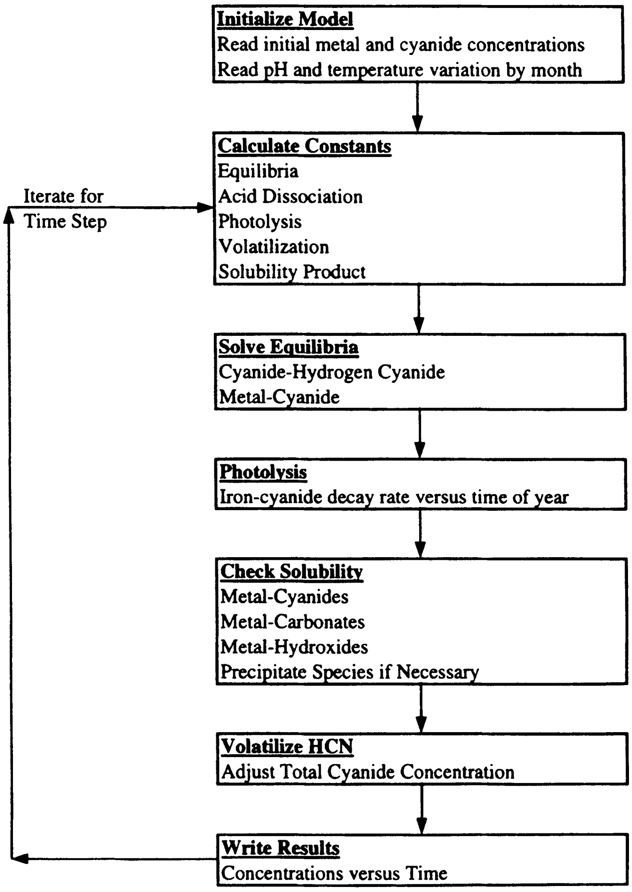


Figure 4 — Structure if cyanide attenuation model.

Tailings impoundment case study

In 1998, the model was used to estimate the rate of loss of cyanide from a tailings impoundment at an inactive mine site. At the time the modeling was completed, solution in the tailings impoundment contained approximately 170 mg/L of total cyanide, which was present almost exclusively as iron cyanide. The situation for this impoundment was unique in that:

- Greater than 98% of the cyanide in the impoundment solution was iron cyanide. Therefore, calibration of the model could proceed specifically for the case of iron-cyanide photolysis. As the rate of hydrogen cyanide volatilization is rapid relative to the rate of iron-cyanide photolysis, the rate of cyanide loss from the impoundment would approximately equal the photolysis rate, and the applicability of GCSOLAR and the

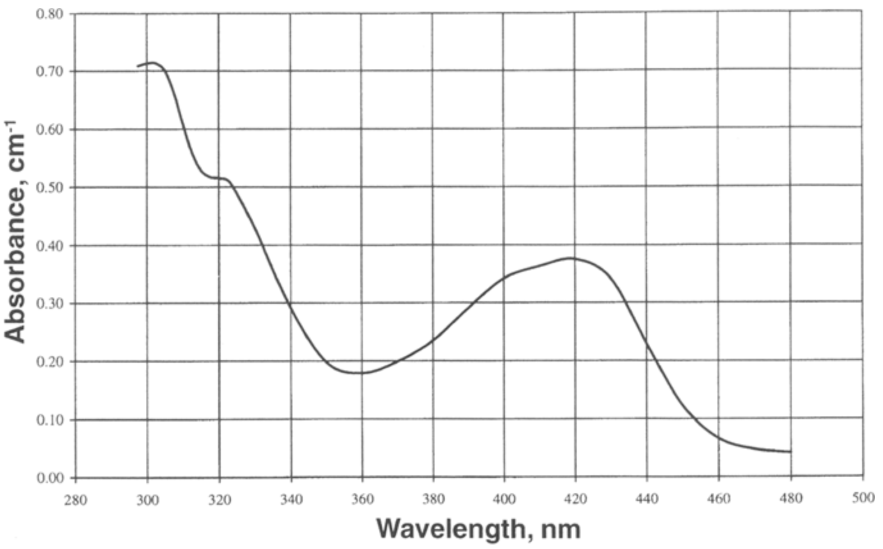


Figure 5 — Impoundment solution absorption spectrum.

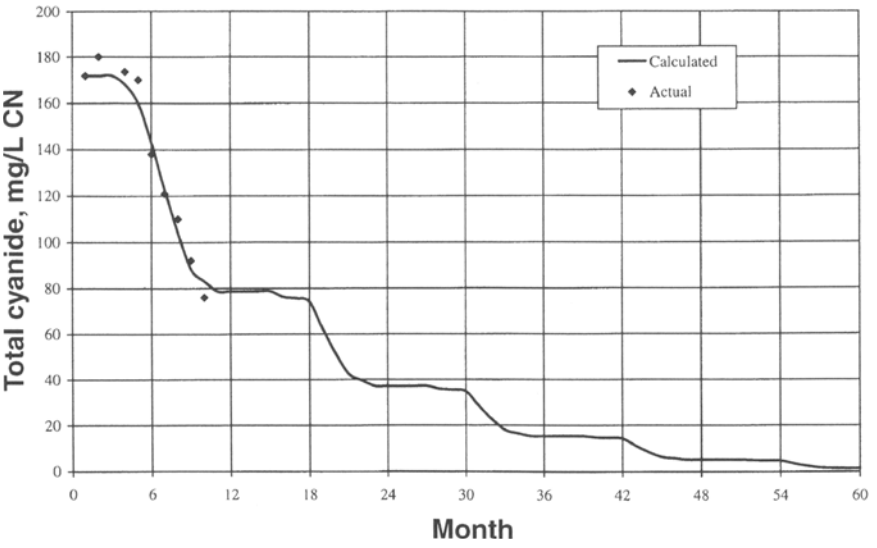


Figure 6 — Total cyanide concentration vs. time.

Table 2 — Impoundment physical and chemical data summary.

Elevation, m	2,200
Average solution depth, m	6.10
Initial total cyanide, mg/L CN	172
Solution pH	8.2 to 8.9

data of Broderius and Smith (1980) could be evaluated. In addition, analytical data and UV spectrographic data for the impoundment solution indicated that only Fe(III) cyanide was present. Therefore, calculations proceeded assuming Fe(II) cyanide was not present in the impoundment solution.

- Tailings were not being disposed in the impoundment. Therefore, the system represented a batch cyanide decay situation rather than a continuous throughput or accumulation situation. This removes some uncertainty associated with the development of an impoundment water-balance model.

Summaries of physical, chemical and weather data for the impoundment under consideration are provided in Tables 2 and 3. The impoundment is located in the northern hemisphere, and, as indicated in Table 3, winter temperatures result in freezing of the pond surface for approximately four to five months per year. In addition to these data, the UV absorbance of the impoundment solution as a function of wavelength is presented in Fig. 5. The absorption spectrum in Fig. 5 is similar in shape to that presented in Broderius and Smith (1980) for Fe(III) cyanide, supporting the assumption that only Fe(III) was present in the impoundment solution. The range of UV of interest is from approximately 300 to 500 nm, because essentially no light less than 300 nm penetrates the earth's atmosphere (Goldman and Home, 1983) and iron cyanides are not photolytically active above 500 nm.

Model calculations for the impoundment were conducted to estimate the total cyanide concentration over a period of five years. A summary of the results is presented in Fig. 6 and Table 4. There is good agreement between the calculated and actual cyanide concentrations presented in Fig. 6 and Table 4, and the model was successful in forecasting the rate of iron-cyanide photolysis for the first eight months of 1998 to within approximately ±10%. However, several years of additional decay data for the impoundment would be required along with weather records to further quantify the accuracy of the model.

The stepwise decrease in total cyanide over the five-year period is a result of the rapid photolysis, which occurs during summer months when the pond is not ice covered followed by periods during the winter when the UV intensity decreases and the pond is ice covered. The calculations indicate that after five years, the total cyanide concentration will decrease from 170 mg/L to less than approximately 10 mg/L.

Calculated photolysis rate constants ranged from 2.62 x 10^{-5} to 21.4 x 10^{-5} $hour^{-1}$ as an average over the full depth of the water body for this specific impoundment. However, it was assumed that when the impoundment is ice covered, the photolysis rate constant is zero. This range of photolysis rate constants corresponds to an Fe(III) cyanide half-life of approximately five months to three years, depending on the time of year, however the average half-life during summer months is approximately six months.

Conclusions

At this time, only field data for iron cyanide has been available for testing of the model, though calibration of the model for copper, nickel and zinc affects on hydrogen cyanide volatilization are underway. In the case study presented for the tailings impoundment, it was desired to estimate the cyanide attenuation rate for use as a reference in planning water management at the site for the next two to five years. For this case, the model was successful at estimating cyanide concentrations for a minimum of about one to two years in advance.

Table 3 — Impoundment weather summary.

Month (1998)	Ice-free surface, %	Water temperature, °C
January	0	0.2
February	0	0.2
March	0	2
April	50	3
May	100	10
June	100	14
July	100	17
August	100	15
September	100	15
October	100	5
November	50	3
December	0	0.2

Table 4 — Impoundment cyanide concentration vs. time.

Month (1998)	Total cyanide, mg/L CN: Actual	Total cyanide, mg/L CN: Calculated
January	172	172
February	180	172
March	–	172
April	173	168
May	170	160
June	138	143
July	121	123
August	110	104
September	92	88
October	76	83
November	–	79
December	–	79

References

Broderius, S., 1973, "Determination of Molecular Hydrocyanic Acid in Water and Studies of the Chemistry and Toxicity to Fish of Metal-Cyanide Complexes," Ph.D. Thesis, Oregon State University.

Broderius, S., and Smith, L.L., 1980, "Direct Photolysis of Hexacyanoferrate Complexes: Proposed Applications to the Aquatic Environment," US Environmental Protection Agency Report 600/3-80-003.

Eastern Research Group, 1997, "Preferred and Alternative Methods for Estimating Air Emissions from Wastewater Collection and Treatment," Final Report, Prepared for the Emission Inventory Improvement Program and the US Environmental Protection Agency, Vol. II, Chapter 5.

Flynn, C.M., and McGill, S.L., 1995, "Cyanide Chemistry — Precious Metals Processing and Waste Treatment," US Bureau of Mines, NTIS Document PB96-117841.

Goldman, C.R., and Home, A.J., 1983, *Limnology*, McGraw-Hill, New York, Chapter 3.

Maracle, K.J., 1992, "Cyanide Regeneration of Gold Mill Barren Solutions Using Hollow Fibre Gas Membranes," Master of Engineering Thesis, McMaster University, Ontario, Canada.

Murphy, K.L. and Robertson, J.L., 1979, "Factors Affecting Natural Degradation of Free and Metal Complexed Cyanides from Gold Milling Effluents," A Literature Review for Fisheries & Environment Canada, Burlington, Ontario, Canada.

Sadek, S.E., Smith, J.D., Watkin, A.T., and Gebel, R., 1996, "Mass transfer of volatile organics from large open basins," *Environmental Progress*, Vol. 15, No. 2, pp. 82-92.

Schmidt, J.W., Simovic, L., and Shannon, E., 1981, "Development studies for suitable technologies for the removal of cyanide and heavy metals from gold milling effluents," *Proceedings of the 36th Industrial Waste Conference*, Purdue University, pp. 831-846.

Simovic, L., 1984, "Kinetics of Natural Degradation of Cyanide from Gold Mill Effluents," Master of Engineering Thesis, McMaster University, Ontario, Canada.

Simovic, L, Snodgrass, W.J., Murphy, K.L., and Schmidt, J.W., 1984, "Development of a model to describe the natural degradation of cyanide in gold mill effluents," *Conference on Cyanide and the Environment*, Tucson, AZ, pp. 413-432.

Simovic, L., and Snodgrass, W.J., 1989, "Tailings pond design for cyanide control at gold mills using natural degradation," *Proceedings from Gold Mine Effluent Treatment Seminars*, Vancouver, British Columbia, Canada, pp. 58-81.

Smith, J.H., Bomberger, D.C., and Haynes, D.L., 1980, "Prediction of the volatilization rates of high-volatility chemicals from natural water bodies," *Environmental Science & Technology*, Vol. 14, No. 11, pp. 1332-1337.

Smith, A. and Mudder, T., 1991, *The Chemistry and Treatment of Cyanidation Wastes*, Mining Journal Books Ltd., London, Chapter 3.

Thomas, R.G., 1990, "Volatilization from water," in *Handbook of Chemical Property Estimation Methods*, Chapter 15, W.J. Lyman, W.F. Reehl and D.H Rosenblatt, eds., Published by American Chemical Society, Washington D.C.

US Environmental Protection Agency, 1988, GCSOLAR Version 1.1 (Available through the Center for Exposure Assessment Modeling, Environmental Research Laboratory, Athens, GA).

US Environmental Protection Agency, 1994, "Air Emissions Models for Waste and Wastewater," EPA Document 453/R94-080A.

Zemaitis, U., Clark, D.M., Rafal, M., and Scrivner, N.C., 1986, *Handbook of Aqueous Electrolyte Thermodynamics*, Design Institute for Physical Property Data, American Institute of Chemical Engineers, New York.

Zepp, R.G., and Cline, D.M., 1977, "Rates of direct photolysis in aquatic environment," *Environmental Science & Technology*, Vol. 11, No. 4, pp. 359-366.